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THE SYNTHESIS AND CHARACTERIZATION OF STEREOREGULAR POLY(ALKYL α-BROMOACRYLATE)S

A Dissertation Presented

By

Keith G. Saunders

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ABSTRACT

The Synthesis and Characterization of Stereoregular
Poly(alkyl α-bromoacrylate)s

(March 1979)

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Isotactic, atactic and syndiotactic polymers of the methyl, ethyl, n-propyl, i-propyl, n-butyl and n-pentyl α-bromoacrylates were synthesized. A procedure was developed in which two steps of the monomer synthesis was consolidated into one. The isotactic polymers were prepared with a "modified Grignard" complex which was composed of the reaction product between methyl magnesium chloride and benzalacetophenone. The polymerization reactions were heterogeneous and anionic in nature and produced polymers with number average molecular weights of between 31,000 and 93,000. The polydispersities were all within the range of 2.99 and 3.35.

Decanoyl Peroxide was employed as a free radical initiator in the polymerization of the atactic polymers. The number average molecular weights were in the 15,000 to 44,000 range. The syndiotactic polymers were synthesized at -40°C with ultraviolet light and benzoin as the photoinitiator. Those polymers generally had the narrowest molecular weight distributions and were between 1.63 and 2.17. The number average molecular weights ranged from 29,500 to 63,000.

A shortcut was developed in the preparation of t-butyl α-bromo-acrylate in which two steps were combined into one. Due to the failure of this monomer to polymerize in solution, it was polymerized only at 50°C in the bulk state with decanoyl peroxide.

The analysis of polymer tacticity was achieved with 19 mHz ^{13}C NMR spectroscopy. Tacticity measurements were conducted for the isotactic, atactic and syndiotactic polymers of all the esters except the t-butyl. Quantitative evaluation of tacticity was obtained from three different carbon resonances: the carbonyl carbon, the quaternary carbon and the backbone methylene carbon. Complete pentad assignments for the carbonyl carbon resonance was achieved for all esters but the i-propyl while the tetrad assignments for the backbone methylene resonance was accomplished for all but the methyl ester. The tetrad values calculated from the experimentally determined pentad contents agreed well with the experimental tetrad values. As a result of insufficient peak separation of the quaternary carbon resonance, complete pentad assignments were obtained for only a few samples.

From an analysis of the m and r sequence distribution, all of the isotactic polymers were found to obey first-order Markovian propagation statistics. The percentage of isotactic triad units for these polymers ranged from 60 for the i-propyl ester to 74 for the n-propyl ester. Both the atactic and syndiotactic polymers displayed near perfect Bernoullian propagation statistics. The atactic samples were moderately syndiotactic and contained rr triad values between 43 and 46%. The polymers synthesized at -40°C had a higher syndiotactic triad content of between 60 and 66%.

All of the poly(alkyl α-bromoacrylate)s were found to undergo a post-polymerization reaction producing γ-butyrolactone rings along the polymer backbone. Evidence for lactone formation was obtained from IR spectroscopy, NMR spectroscopy and pyrolysis gas chromatography. An absorption band at 1798 cm^{-1} arising from the lactone carbonyl group was used in conjunction with the ester carbonyl absorption band at 1730 cm^{-1} to quantitatively determine the degree of lactone formation.

The syndiotactic polymers exhibited significantly higher lactonization rates than the corresponding isotactic polymers under identical conditions. The lactone contents differed between 12 and 16% for an isotactic-syndiotactic pair. These differences were attributed to the differences in the molecular configurations for the stereo-isomers. The order of lactonization increased in the following order: methyl, n-pentyl, n-butyl, ethyl, n-propyl and i-propyl for both the isotactic and syndiotactic samples. The degree of lactone formation ranged from 25 to 39% for the isotactic esters and 37 to 55% for the syndiotactic esters after 4 hours in 1,1,2,2-tetrachloroethane at 80°C.

A mechanism involving a concerted one-step reaction was proposed to explain the different reactivities of the ester groups. The lactonization reactions followed first-order kinetics for reaction times of 120 minutes or less.

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CHAPTER I

HISTORICAL BACKGROUND

All previous investigations involving poly(alkyl α-bromoacrylate)s were undertaken primarily to evaluate the percentage of head to head versus head to tail placement in free radical polymerization[1-4]. The polymers studied were the methyl, ethyl and s-butyl esters and the results indicated that the head to tail structure predominated, similar to the poly(alkyl α-chloroacrylate)s[1,2].

During the course of these investigations poly(methyl α-bromoacrylate) was found to undergo partial lactonization after treatment with concentrated sulfuric acid in alcohol solution[4]. Under similar conditions poly(methyl α-chloroacrylate) required a substantially longer time before the appearance of lactone groups. The presence of these lactone rings was inferred from the appearance of a strong infrared absorption band at 1795 cm^{-1} attributable to the carbonyl group of the lactone ring. Similar evidence for lactone formation was reported for both poly(α-chloroacrylic acid) and poly(α-bromoacrylic acid) but without the need for acidic conditions[5,6]. In addition, a slight correlation between tacticity and the conversion to lactone units was observed for stereoregular poly(α-chloroacrylic acid). The lactonization reactions were conducted in the solid state where the isotactic polymer exhibited a greater tendency to form lactone rings than the syndiotactic polymer. Although poly(α-bromoacrylic acid) was shown to have a higher rate of lactone formation than poly(α-chloroacrylic acid), the effect

of tacticity was not investigated. However, the possibility for lactonization under neutral conditions has not been investigated for any of the poly(alkyl α-bromoacrylate)s.

While there has been no effort directed toward the preparation of stereoregular poly(alkyl α-bromoacrylate)s a considerable amount of attention has been focused on the preparation of stereoregular poly(alkyl α-chloroacrylate)s, particularly poly(methyl α-chloroacrylate)[7-12]. Studies from this laboratory have included those by Wesslen and Lenz[13] on poly(ethyl α-chloroacrylate) and by Dever *et al.*[14] who also studied the corresponding methyl and isopropyl esters. These investigations were undertaken in order to prepare a wide range of stereoregular polymers where the influence of the steric structure on the glass transition temperature could be studied.

Initially, it was expected that stereoregular poly(alkyl α-chloroacrylate)s could be synthesized in a manner similar to the corresponding poly(alkyl methacrylate)s. In many instances it had been demonstrated that high molecular weight, highly syndiotactic poly(methyl methacrylate) could be prepared by a variety of techniques[15-23]. Abe and co-workers achieved high molecular weight poly(methyl methacrylate) containing over 90% syndiotactic triads using triethyl aluminum and titanium tetrachloride[15]. In polar solvents both n-butyllithium and n-amyl sodium produced syndiotactic polymers, although a higher degree of syndiotactic units were achieved by Roig and co-workers with biphenyllithium in glyme at -78°C[16].

A larger variety of initiators has been successfully used in the preparation of isotactic poly(methyl methacrylate)[16-18,25-29].

Initiators such as n-butyllithium[26] and phenyl magnesium bromide[26-29] in non-polar solvents at 0 and -78°C initiated the polymerization of methyl methacrylate into a polymer containing approximately 80% isotactic triads. A Ziegler type heterogeneous complex of n-butyllithium and titanium tetrachloride in non-polar solvents polymerized t-butylacrylate into a crystalline, isotactic polymer[30]. A similar system consisting of vanadium tetrachloride and tri-isobutyl aluminum was employed by Gaylord and Mark in the preparation of isotactic poly(methyl methacrylate) although it was found that a complexing agent such as tetrahydrofuran or diethyl ether was required[31]. In general, the use of Grignard reagents and organolithium compounds in non-polar solvents at low temperatures resulted in polymers containing 70-90% isotactic triads.

In view of the large variety of initiators capable of producing highly syndiotactic poly(methyl methacrylate) similar investigations were undertaken to synthesize syndiotactic poly(methyl α-chloroacrylate)[7-10, 12-14]. All of the initiators employed including: organolithium, organosodium, Grignard reagents and Ziegler-Natta type systems proved to be ineffective. Wesslen and Lenz[13] demonstrated this with n-butyl magnesium bromide, phenyl magnesium bromide, n-butyllithium and fluorenyllithium in both polar and non-polar solvents at various temperatures. While tacticities of 65% were achieved in several cases, the molecular weights were all very low. However, it was shown by Matsuzaki and co-workers[10] that methyl α-chloroacrylate could be polymerized free radically at -78°C into a highly syndiotactic form using the method first developed by Fox *et al.*[26] on methyl methacrylate. Utilizing this technique, Dever and co-workers prepared polymers of the

methyl and ethyl α-chloroacrylates containing 63 and 78% syndiotactic triads, respectively, at -50°C with the molecular weights in excess of 100,000[14].

Anionic polymerization of alkyl α-chloroacrylate monomers has yielded only low molecular weight polymers of significantly less isotacticity than the corresponding methyl methacrylate polymers[7-10, 12-14]. The initiators showing essentially no stereospecific activity were: organolithium and organosodium compounds, Grignard reagents and Ziegler-Natta catalysts. Uryo, Ito and Matsuzaki[9] prepared isotactic poly(methyl-α-chloroacrylate(mm=0.68) with phenyl magnesium bromide in toluene at 0°C. It was of very low molecular weight and is the only instance where a Grignard reagent was effective in producing an isotactic polymer, although subsequent investigations by the same authors[9] as well as others[13,14] could not duplicate the result. An extensive investigation by Dever and co-workers[14] with a wide variety of anionic initiators including: n-butyllithium, t-butyllithium, phenyllithium, phenyl magnesium bromide and fluorenyllithium produced polymer tacticities of less than 30% on a triad basis as well as low molecular weights. Furthermore, organosodium and Ziegler-Natta type systems yielded moderately to predominantly syndiotactic poly(methyl α-chloroacrylate) which was in complete contrast to previous work with poly(methyl methacrylate).

Anionic polymerization of the alkyl α-haloacrylates may be hindered by the occurrence of substitution or elimination reactions at the α-halogen on the polymer backbone. Reactions could occur with either the initiating or polymeric anion, resulting in a halogen deficiency in the polymer and premature termination. Polymers having fairly low

molecular weights would result as was reported for many of the previous investigations.

The most significant advancement in this area was that by Breslow and Kutner[11,25] who polymerized methyl methacrylate and methyl α-chloroacrylate into highly isotactic, crystallizable polymers. This was the first highly isotactic α-chloroacrylate polymer of high molecular weight prepared by any means. Although no NMR spectra were shown, it was stated that only isotactic units were detectable.

The type of initiating system was termed a "modified Grignard complex" and consisted of the 1,4 reaction product of an α- β-unsaturated ketone, such as benzalacetophenone, and a Grignard reagent. Typical Grignard reagents found to be effective were: ethyl magnesium chloride, ethyl magnesium bromide and phenyl magnesium bromide. The polymerizations were conducted in solvents such as heptane, toluene or diethyl ether at temperatures from -30 to 68°C. The authors claimed that only the molecular weight and conversion and not the stereoregularity were altered by changes in solvent, although no spectral evidence was presented. It was stated that excess benzalacetophenone decreased the activity of the catalyst complex causing a decrease in the molecular weight and apparently the low molecular weight poly(methyl α-chloroacrylate) prepared by Uryu, Ito and Matsuzaki demonstrated this. When the Grignard reagent was used in excess, the catalyst complex consisted of the desired catalyst as well as other species which were less effective in promoting isotactic placement. Subsequently, several other groups duplicated these results with methyl α-chloroacrylate[8-14], ethyl α-chloroacrylate[7-9,14] and isopropyl α-chloroacrylate[14]. The polymers

generally contained between 60 and 80% isotactic units with molecular weights in excess of 40,000.

Dever and co-workers[14] prepared poly(methyl α-chloroacrylate) containing 65% isotactic units on a triad basis with a molecular weight of 40,000 using the modified Grignard complex. In the same manner, ethyl α-chloroacrylate was polymerized into a high molecular weight (350,000) polymer of similar tacticity and appeared by the x-ray diffraction pattern to be the more crystalline of the two. Somewhat poorer results were achieved with isopropyl α-chloroacrylate where a polymer containing only 50% isotactic units could be synthesized. In almost all instances the chlorine contents were very close to those expected theoretically.

The tacticities of the stereoregular poly(methyl α-chloroacrylate)s prepared to date[7-11, 13, 14] have been determined primarily by 100 mHz proton nuclear magnetic resonance spectroscopy according to the assignments of Matsuzaki and co-workers[10]. Quantitative stereochemical information was possible from measurement of the methoxyl resonance centered at 3.8 ppm downfield from tetramethylsilane (TMS). The methoxyl resonance consisted of a triplet where the downfield contribution was assigned to the isotactic triads, the upfield contribution assigned to the syndiotactic triads and the intermediate portion assigned to the heterotactic triads. These assignments were identical to those of the α-methyl resonance of poly(methyl methacrylate)[18]. Tetrad assignments for the backbone methylene protons were also achieved by Matsuzaki and co-workers from the 100 mHz spectra of atactic and syndiotactic poly(methyl α-chlorocrylate-β-d_1)[9]. Unfortunately, due to excessive peak overlap of the non-dueterated polymer spectra, it was not possible to

interpret the tetrad structure quantitatively even though qualitative information was possible. In addition, Dever et al.[32] successfully resolved all eighteen tetrad peaks with the use of 300 mHz proton nuclear magnetic resonance spectroscopy.

The assignments for the ethyl ester resonance of poly(ethyl α-chloroacrylate) were determined by Wesslen and Lenz with 220 mHz nuclear magnetic spectroscopy[33]. Only qualitative evaluation of tacticity was possible by Dever et al.[14] using 100 mHz nuclear magnetic resonance due to insufficient resolution of the set of nine overlapping resonance peaks. Subsequently, quantitative assignments for all the tetrad peaks as well as the nine possible peaks for the ester CH_3-protons were determined by 300 mHz nuclear magnetic resonance spectroscopy[32]. In a similar manner, assignments were made for the methyl resonance of poly(isopropyl α-chloroacrylate) which was composed of three doublets each corresponding to the isotactic, heterotactic and syndiotactic components of which only two were resolvable with 100 mHz nuclear magnetic resonance spectroscopy[14].

The primary purpose of this investigation was to synthesize a wide range of stereoregular poly(alkyl α-bromoacrylate)s where the influence of the stereostructure on the glass transition temperature could be studied. The fact that steric configuration effected T_g in the case of α,α-disubstituted vinyl polymers and not in monosubstituted vinyl polymers was clearly pointed out by Karasz, Blair and O'Reilly[34]. The poly(alkyl methacrylate) series which had been studied extensively showed this variation exceptionally well[35]. Karasz and MacKnight[36] rationalized this empirical effect theoretically by employing the

Gibbs-Dimarzio glass transition theory as a foundation[37] where they considered that variations in the glass transition temperature (T_g) were due to intramolecular effects caused by changes in the steric configuration and were independent of intermolecular effects caused by changes in the ester group. This treatment resulted in a general expression relating the differences in T_g for an isotactic-syndiotactic pair of a disubstituted vinyl polymer:

$$T_g \text{ (syn)} - T_g \text{ (iso)} = 0.59 \text{ (e/k)} \qquad (1)$$

where e is the flex energy difference for the stereo-isomers resulting from configurational changes and k is the Boltzman constant. The preceeding relationship enabled one to determine the differences in T_g for a pair of stereo-isomers solely by knowing the value of e. Since the glass transition temperatures for both stereo-isomers were experimentally available for poly(methyl methacrylate), the value of 0.59 (e/k) was calculated to be 112°C. This value would then correspond to any poly(alkyl methacrylate) pair with the same ester group and thus;

$$T_g \text{ (syn)} - T_g \text{ (iso)} = 112°C. \qquad (2)$$

should hold for any such pair. Considering that e was a function of the α-substituent size and that the methyl group and the chlorine atom were of a similar size (Van der Waals radius), led Karasz and MacKnight to postulate that the glass transition temperature differences between a syndiotactic and isotactic pair of the poly(alkyl α-chloroacrylate)s

should be similar to the poly(methyl methacrylate)s.

Consequently, work was undertaken in this laboratory to prepare stereoregular poly(alkyl α-chloroacrylate)s[11,12] as previously described. Glass transition differences between syndiotactic and isotactic pairs of 92, 83, and 68°C for the methyl, ethyl and isopropyl esters, respectively, were measured by differential scanning calorimetry. These values were somewhat lower than the value of 112°C predicted by the theory but could be rationalized by the increased intermolecular forces arising from the more polar chlorine atom. Furthermore, it was concluded that the intramolecular (tacticity) effects and the intermolecular effects were not completely independent of each other, as was presumed in the theory.

In the present investigation, it was desired to investigate another series of highly stereoregular α,α-disubstituted vinyl polymers. The poly(alkyl α-bromoacrylate) series was the choice because of the larger size and lower degree of polarity of the bromine as compared to the chlorine atom. The polymers to be studied will include the: methyl, ethyl, n-propyl, i-propyl, n-butyl, t-butyl, and n-pentyl esters.

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CHAPTER II

SYNTHESIS AND POLYMERIZATION OF POLY(ALKYL α-BROMOACRYLATE)S

Sources and Purification of Reagents

Solvents (Fisher Chemical Co., Aldrich and Eastman Organic Chemicals - reagent grade or better).

n-Heptane and diethyl ether. They were distilled once, refluxed over metallic sodium and then redistilled into a flask containing metallic potassium. After 2-4 hours of additional reflux under purified N_2, the solvent was redistilled from the drying agent into the predried reaction vessel.

Toluene, benzene, chloroform and tetrachloroethane. All were spectral grade and were distilled under purified N_2 into a container containing molecular sieves.

Tetrahydrofuran and dioxane. They were distilled from potassium hydroxide under purified N_2 into a suitable reaction vessel.

Organic Reagents

Acrylic acid, methylacrylate and n-butylacrylate. (Polysciences, Inc.) They were used as received.

Thionyl chloride. (Eastman Organic Chemicals) This was used as received.

Bromine. (Fisher Scientific Co.) This was used as received.

Quinoline. (Eastman Organic Chemicals) This was distilled under purified N_2 prior to use.

Ethanol, n-propanol, i-propanol and n-pentyl alcohol. (Matheson, Coleman and Bell) They were distilled immediately before use.

t-Butyl alcohol. (Eastman Organic Chemicals) This was refluxed over CaH_2 for 24 hours and then distilled directly into the reaction vessel.

Initiators

Decanoyl peroxide. (Lucidol, Inc.) This was used as received.

Benzoin and benzophenone. (Eastman Organic Chemicals) They were recrystallized twice from methanol at 0°C and dried under vacuum at 30°C.

Benzalacetophenone. (ICN Pharmaceuticals, Inc.) This was recrystallized twice from petroleum ether, grade F, and dried under vacuum at 30°C.

Grignard reagents. (Alfa Inorganics) Methyl magnesium chloride and ethyl magnesium chloride were used as received as 3M solutions in tetrahydrofuran.

Alkyl 2,3-Dibromopropionate Synthesis

The primary and secondary esters of the poly(alkyl α-bromoacrylate)s were prepared by the method of Marvel and Cowan initially developed for methyl α-bromoacrylate[1]. Only the methyl, ethyl, and s-butyl esters had been previously prepared[1,2]. In this procedure, the corresponding alkyl 2,3-dibromopropionates were used as intermediates. The synthesis consisted of three steps: esterification of acrylic acid, bromination of the vinyl ester to form the alkyl 2,3-dibromopropionate and dehydrobromination. Quinoline, which was used to remove hydrogen bromide,

abstracted exclusively the β-bromine and the α-hydrogen and produced the α-bromoacrylate monomer in a 70-85% yield. In this investigation, methyl α-bromoacrylate and n-butyl α-bromoacrylate were synthesized from the corresponding alkyl acrylates, i.e., methyl acrylate and n-butyl acrylate, eliminating the first step.

Methyl 2,3-dibromopropionate[2]. 86g (1 mole) of methyl acrylate was dissolved in 150 mls of distilled methanol in a 1 liter, 1 neck boiling flask. Cold bromine (60 mls, 2.3 moles) was added dropwise over a one-hour period with rapid magnetic stirring. The reaction temperature was maintained below 50°C with an ice bath to minimize any possible thermal polymerization. Since a small excess of bromine was used in the reaction, the solution remained a light reddish color. After allowing the reaction to stand overnight, the methanol was distilled from the reaction mixture and then the product, a colorless liquid, was removed by vacuum distillation. Yield: 1915g (0.8 mole) methyl 2,3-dibromopropionate, 80%; B.P.: 92-95°C (20 mm) [Lit[2]: 96-98°C (22 mm)].

Ethyl 2,3-dibromopropionate[3]. The first step in the synthesis of this material involved the preparation of ethyl acrylate from acrylic acid. This was accomplished by means of a conventional acid catalyzed esterification. Typically, 72g (1 mole) of acrylic acid was dissolved in 250 mls of dry ethanol containing 2 mls of concentrated hydrochloric acid and then refluxed for 24 hours. It was found that the esterification could be pushed to near completion using an azeotropic distillation to remove the esterification product, water. Benzene,

which formed a ternary azeotrop with ethanol and water, was utilized to remove the water as if formed. After removal of the water, ethanol and benzene from the system, ethyl 2,3-dibromopropionate was prepared without isolation of the product, ethyl acrylate. The bromination reaction was carried out as before using 60 mls (2.3 moles) bromine. The remaining ethanol and benzene were removed by normal distillation followed by ethyl 2,3-dibromopropionate under reduced pressure. Overall yield: 190g (0.75 moles) of ethyl 2,3-dibromopropionate, 75%; B.P.: 80-82°C (5 mm) [Lit[3]: 98.5-99.5°C (10 mm)].

n-Propyl 2,3-dibromopropionate[4]. This compound was also prepared from acrylic acid but a shortcut in the synthetic procedure was developed where the esterification and bromination reactions were effectively consolidated into one. Thus, 72g (1 mole) of acrylic acid was combined with 250 ml of distilled n-propyl alcohol in a 1 liter, 1 neck boiling flask followed by the addition of 60 mls (2.3 moles) of cold bromine. The reaction was left overnight, 75 mls of benzene was added and then an azeotropic distillation was carried out for 24 to 36 hours to remove the esterification product, water. The product, n-propyl 2,3-dibromo-propionate, was distilled out under reduced pressure after first removing the excess benzene and n-propyl alcohol. Yields in excess of 90% were achieved in all cases. Apparently, the formation of hydro-bromic acid from bromine and water in the system provided an excellent catalyst for the esterification reaction and eliminated the need for an external catalyst. This procedure was used with excellent results for the preparation of other n-alkyl and s-alkyl esters in this

investigation. Overall yield: 235g (0.86 moles) of n-propyl 2,3-dibromopropionate, 86%; B.P.: 78-80°C (2 mm) [Lit[4]: 149-150 °C (60 mm)].

i-Propyl 2,3-dibromopropionate[5]. The novel technique developed for the preparation of n-propyl 2,3-dibromopropionate was also employed in the synthesis of i-propyl 2,3-dibromopropionate. The only required change was the substitution of i-propyl alcohol for n-propyl alcohol. It is important to point out that it was necessary only to distill the alcohol and not to remove all traces of water. The overall yield for the preparation of this ester was comparable (80%) with the n-propyl ester. B.P.: 143-146°C (60 mm) [Lit[5]: 115°C (35 mm)].

n-Butyl 2,3-dibromopropionate[6]. 128g (1 mole) of n-butyl acrylate was added to 150 mls of distilled n-butyl alcohol in a 1 liter, 1 neck boiling flask followed by the dropwise addition of 60 mls (2.3 moles) of cold bromine. The temperature was kept below 50°C and rapid magnetic stirring was used continuously. After the reaction was left overnight, the excess n-butyl alcohol was distilled off and the product, a colorless liquid, was removed by vacuum distillation. Yield: 245g (0.85 moles) of n-butyl 2,3-dibromopropionate, 85%; B.P.: 120°C (5 mm) [Lit[6]: 163-164°C (60 mm)].

n-Pentyl 2,3-dibromopropionate. In a 1 liter, 1 neck boiling flask was placed 86g (1 mole) of acrylic acid and 300 mls distilled n-pentyl alcohol (n-amyl alcohol). To this was added 60 mls (2.3 moles) of cold bromine with continuous magnetic stirring. Again, the temperature was kept below 50°C to avoid the formation of poly(acrylic acid). An

azeotropic distillation with benzene (75 mls) was conducted as before to remove water. After distilling the benzene and excess n-amyl alcohol from the reaction mixture, the product was distilled out under vacuum. The overall yield for this reaction was somewhat lower than for the other esters but was still satisfactory. Overall yield: 215g (0.71 moles) of n-pentyl 2,3-dibromopropionate, 71%; B.P.: 108-110°C (1 mm).

Methyl 2,3-dibromopropionate and n-butyl 2,3-dibromopropionate were generally prepared from the corresponding alkyl acrylates but small scale syntheses from acrylic acid and the appropriate alcohol produced the propionates in yields 78 and 74%, respectively. Figures 2-1 through 6 show the 90 mHz nuclear magnetic resonance spectra for the alkyl 2,3-dibromopropionates.

Monomer Synthesis

Methyl α-bromoacrylate[1]. In a 500 ml, 1 neck boiling flask was placed 100g (0.4 mole) of methyl 2,3-dibromopropionate. Following a 20-minute purge with prepurified nitrogen, 65g (0.5 mole) of freshly distilled quinoline was added slowly with the formation of a reddish-brown color. At this point, gentle heating was applied and a dark reddish-brown precipitate materialized, presumably quinoline hydrobromide. Methyl α-bromoacrylate, a colorless liquid, was immediately distilled from the reaction mixture under vacuum. Yield: 55g (0.33 mole) of methyl α-bromoacrylate, 83%; B.P.: 80-82°C (60 mm) [Lit: 72-74°C (78 mm)] $d^1 = 1.61$.

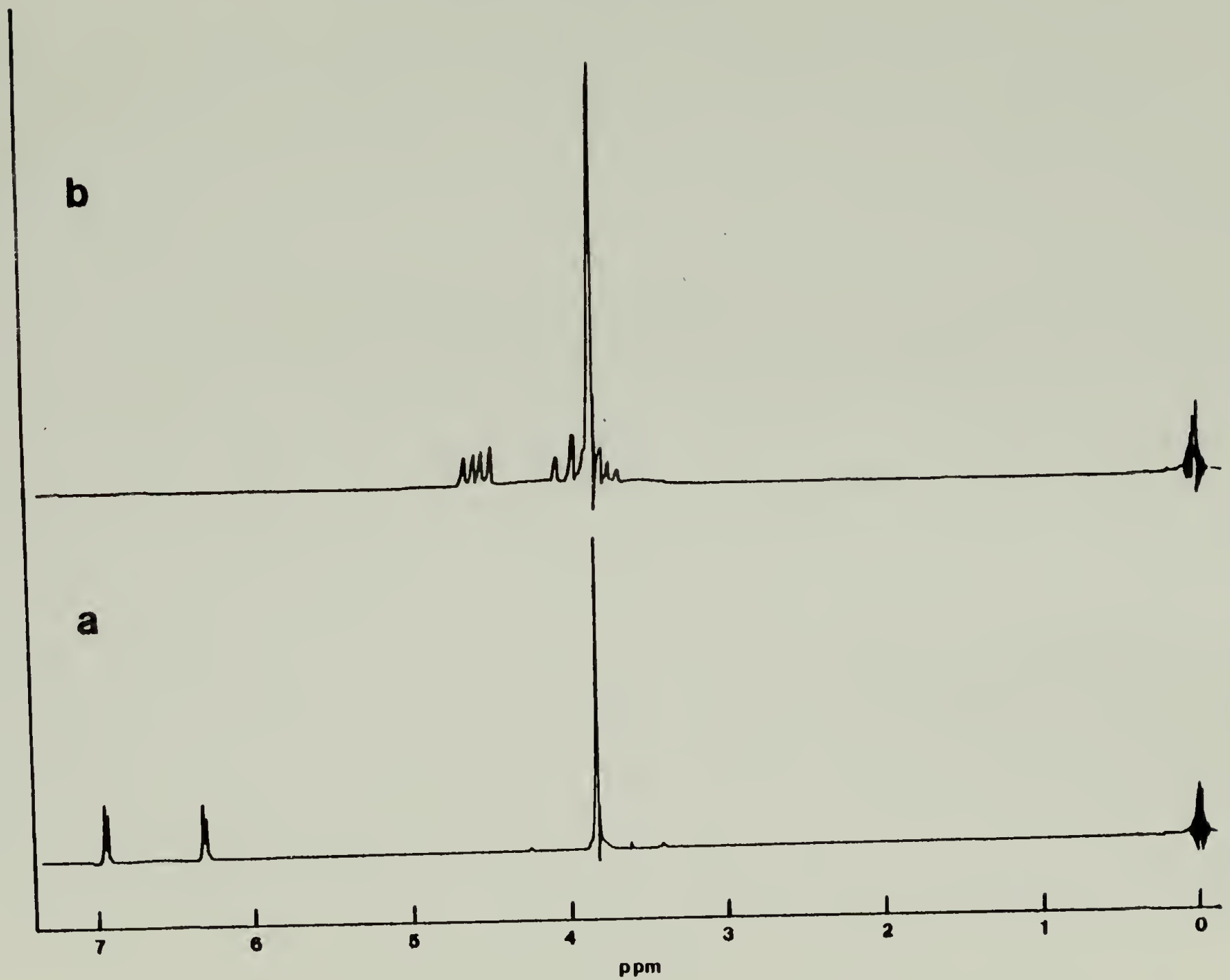


Figure 2-1. Proton NMR Spectra of (a) Methyl α-bromo-acrylate and (b) Methyl 2,3-dibromopropionate Recorded at 35°C is CCl_4

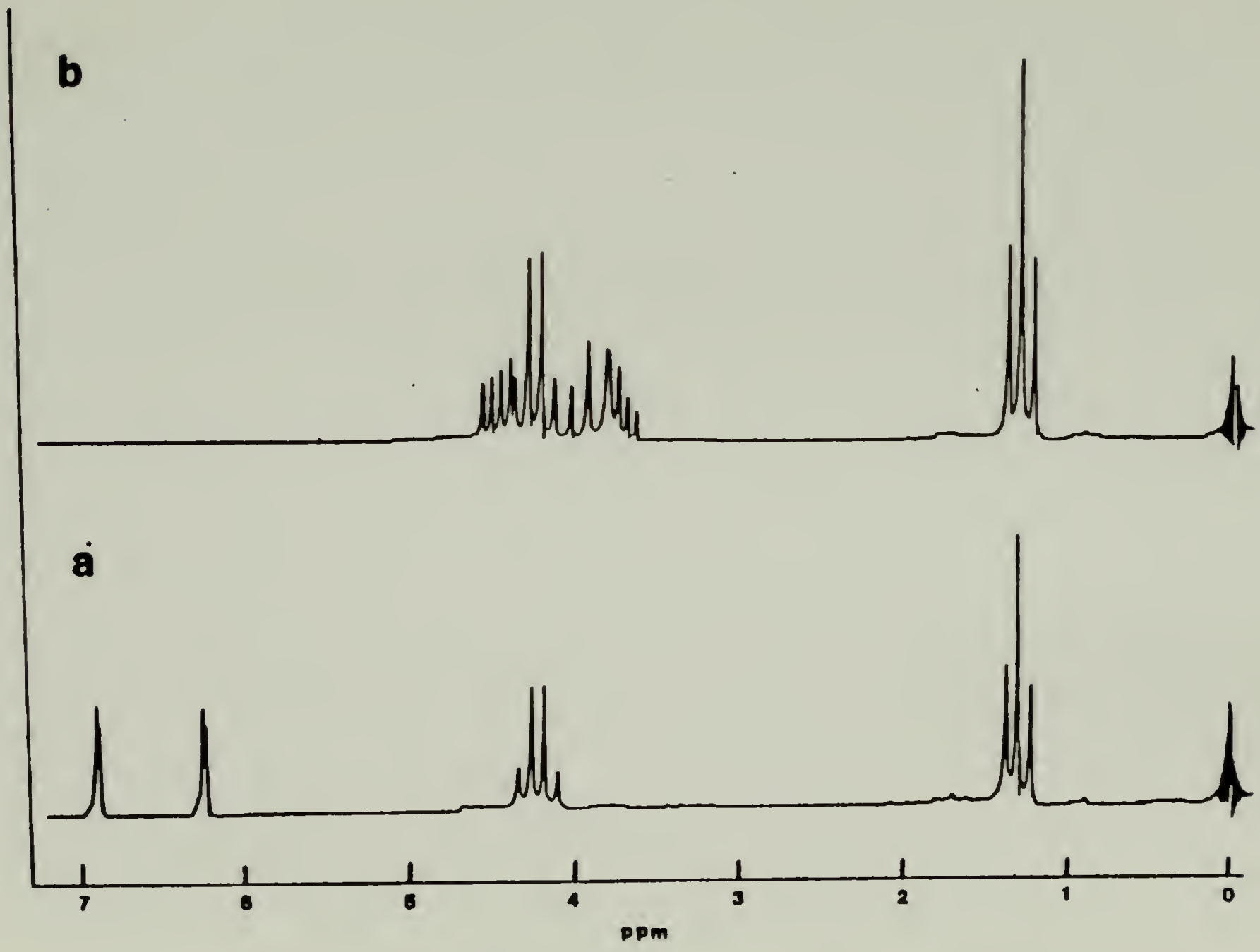


Figure 2-2. Proton NMR Spectra of (a) Ethyl α-bromoacrylate and (b) Ethyl 2,3-dibromopropionate Recorded at 35°C in CCl_4

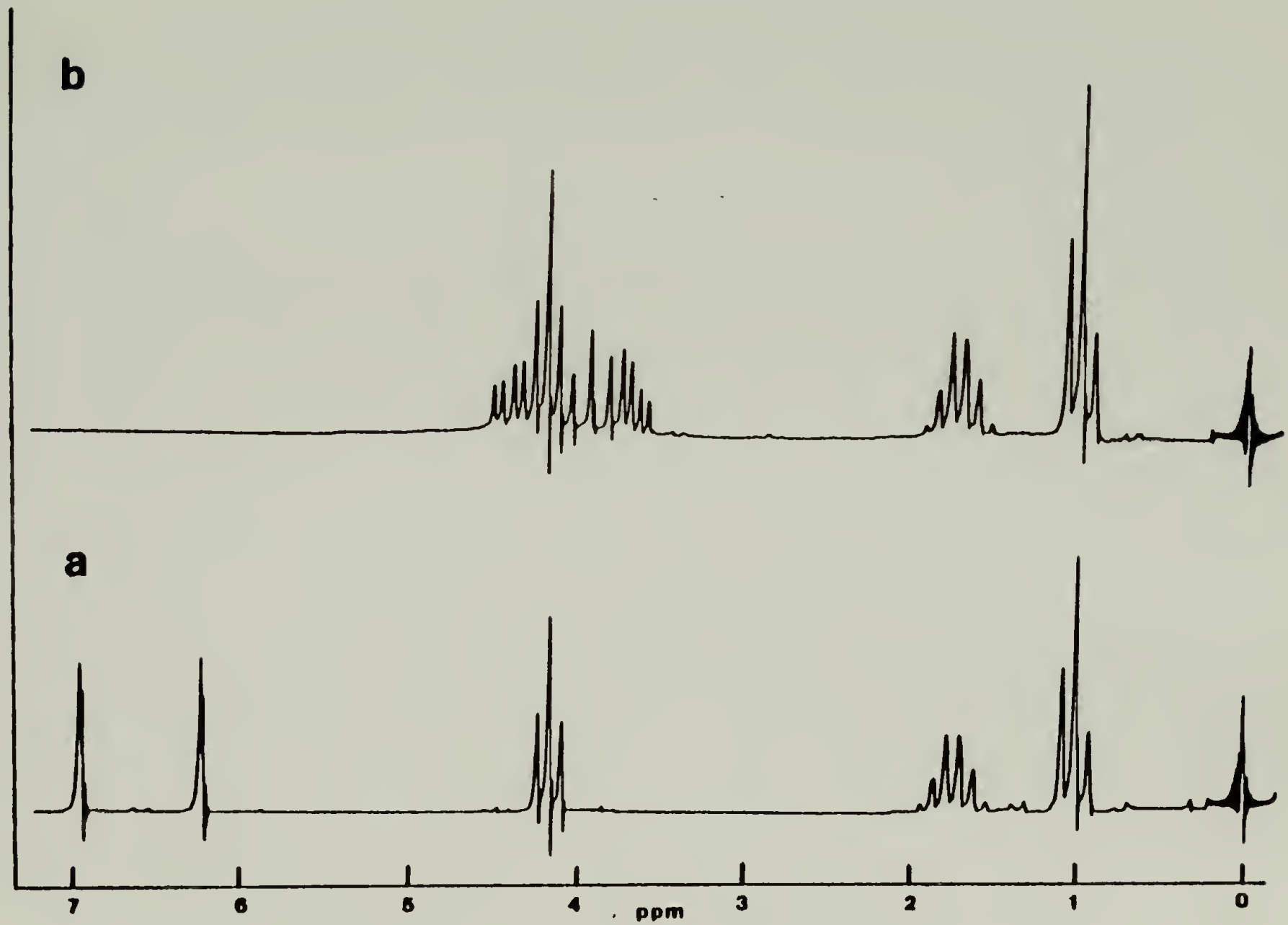


Figure 2-3. Proton NMR Spectra of (a) n-Propyl α-bromoacrylate and (b) n-Propyl 2,3-dibromopropionate Recorded at 35°C in CCl_4

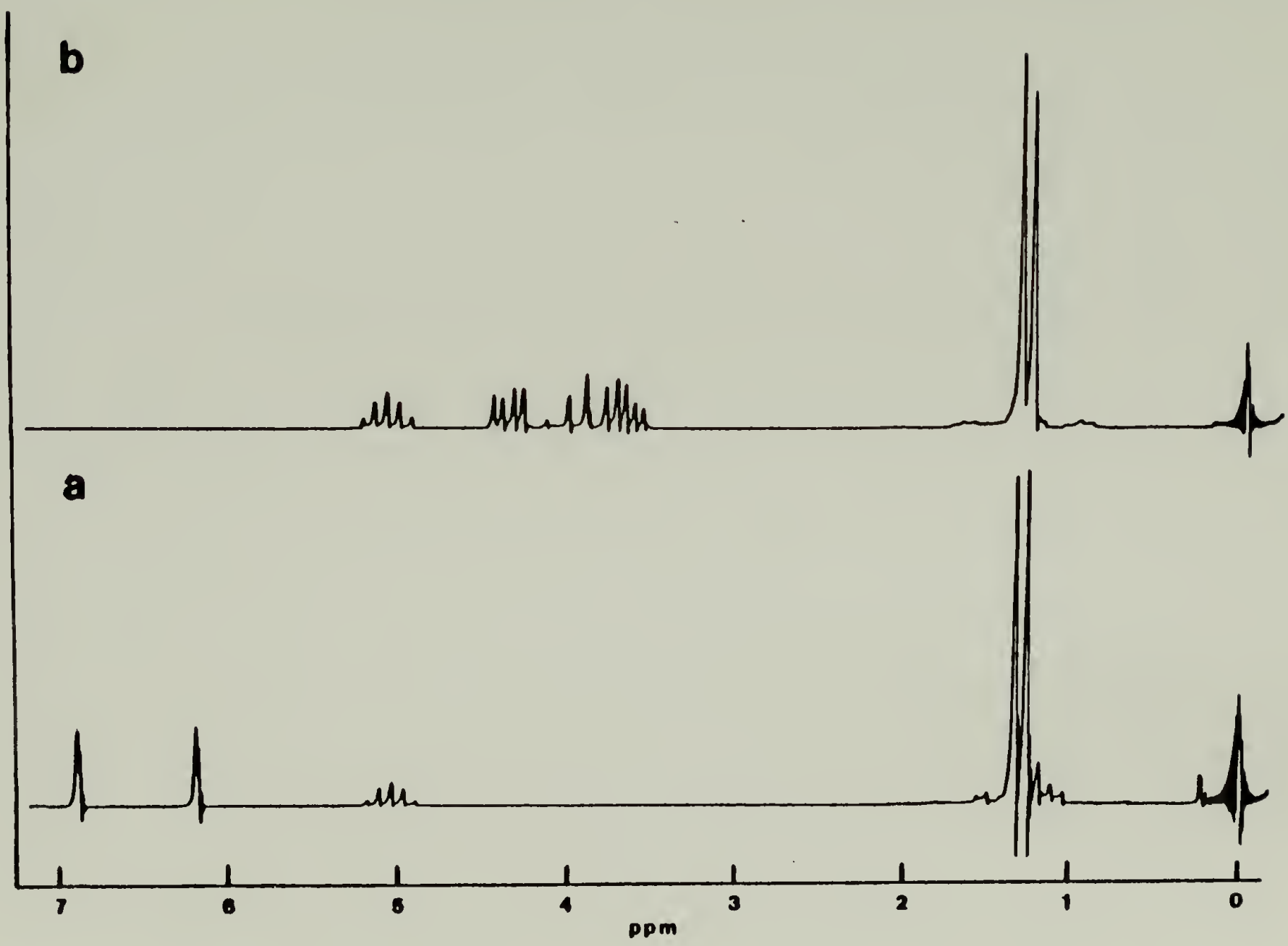


Figure 2-4. Proton NMR Spectra of (a) i-Propyl α-bromoacrylate and (b) i-Propyl 2,3-dibromopropionate Recorded at 35°C in CCl_4

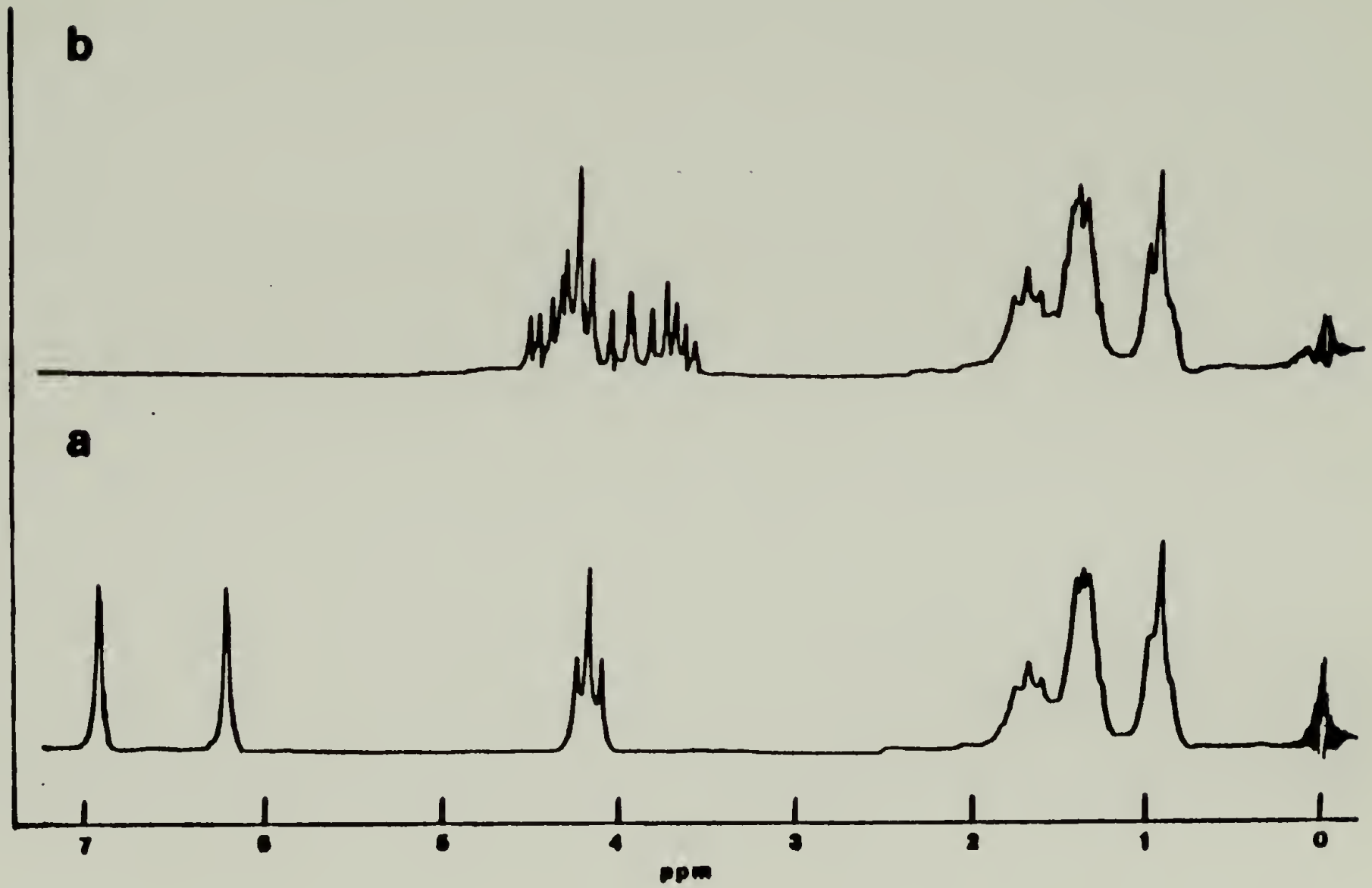


Figure 2-5. Proton NMR Spectra of (a) n-Butyl α-bromoacrylate and (b) n-Butyl 2,3-dibromopropionate Recorded at 35°C in CCl_4

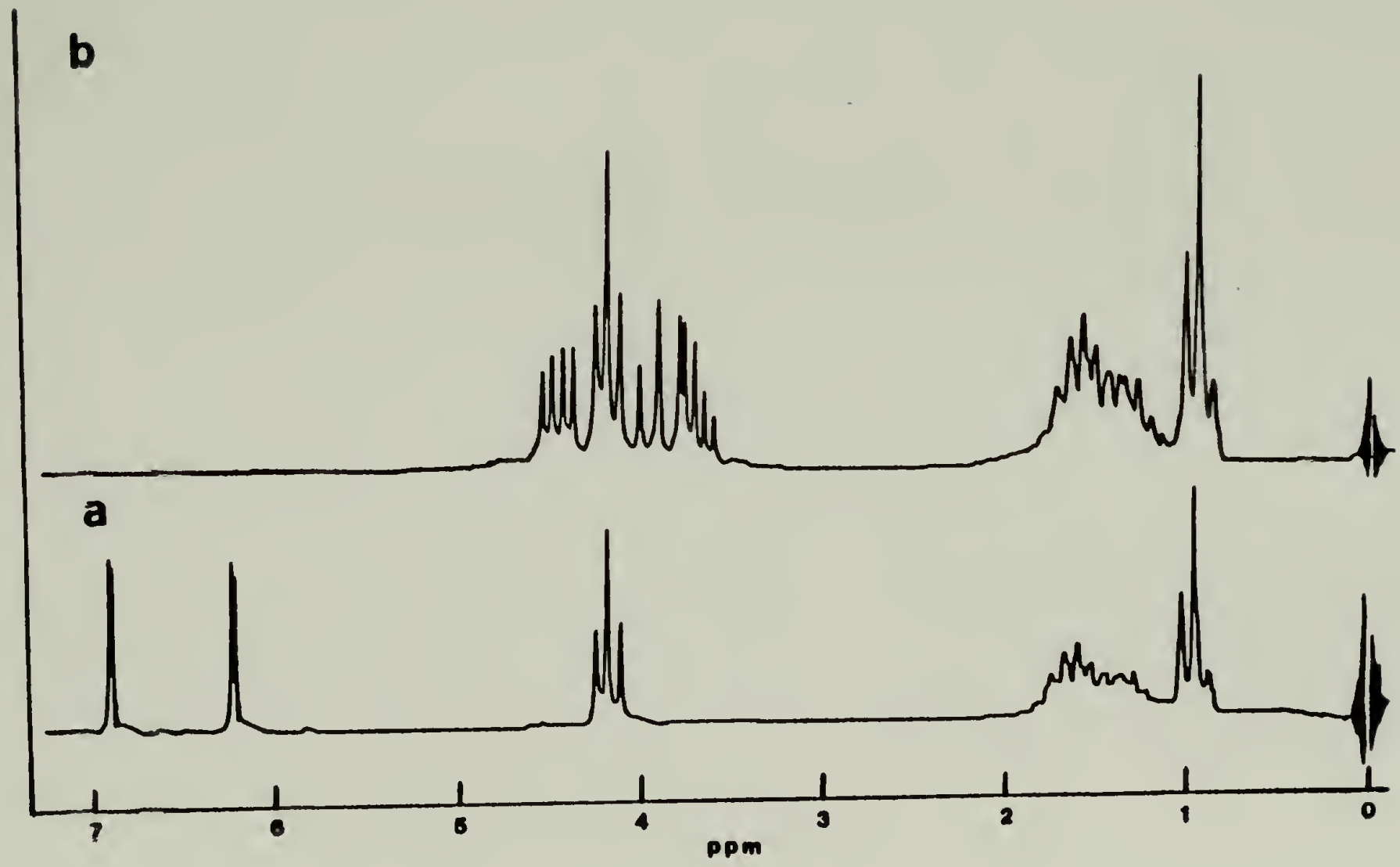


Figure 2-6. Proton NMR Spectra of (a) n-Pentyl α-bromoacrylate and (b) n-Pentyl 2,3-dibromopropionate Recorded at 35°C in CCl_4

Ethyl α-bromoacrylate[2]. In a similar manner, 105g (0.4 mole) of ethyl 2,3-dibromopropionate was reacted with 65g (0.5 mole) freshly distilled quinoline. Yield: 62g (0.34 mole) of ethyl α-bromoacrylate, 86%; B.P.: 60-62 °C (20 mm) [Lit: 63.5-65°C (15 mm)], d^2 = 1.458.

n-Propyl α-bromoacrylate. 110g (0.4 mole) of n-propyl 2,3-dibromopropionate was treated with 65g (0.5 mole) freshly distilled quinoline yielding 52g (0.27 mole) of n-propyl α-bromoacrylate, 67%; B.P.: 79-81°C (22 mm), d = 1.357.

i-Propyl α-bromoacrylate. The exact quantities as for the n-propyl ester were used resulting in a yield of 49g (0.25 mole) of i-propyl α-bromoacrylate, 63%; B.P.: 73-75°C (20 mm), d = 1.296.

n-Butyl α-bromoacrylate. 115g (0.4 mole) of n-butyl 2,3-dibromopropionate was combined with 65g (0.5 mole) of freshly distilled quinoline to give 61g (0.30 mole) of n-butyl α-bromoacrylate, 74%; B.P.: 94-96°C (20 mm), d = 1.321.

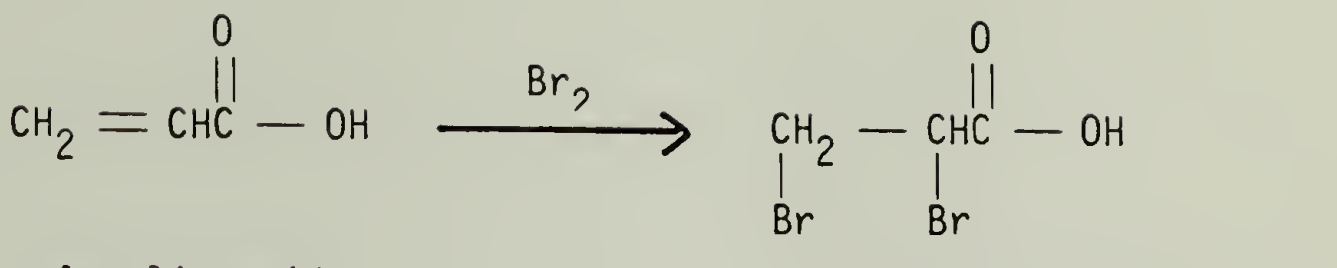
n-Pentyl α-bromoacrylate. Reacted together were 120g (0.4 mole) of n-pentyl 2,3-dibromopropionate and 65g (0.5 mole) of freshly distilled quinoline to produce 64g (0.29 mole) of n-pentyl α-bromoacrylate, 73%; B.P.: 113-115°C (20 mm), d = 1.224.

t-Butyl α-bromoacrylate. The preparation of this monomer, the t-butyl ester, could not be achieved with the previous technique due to the reactive nature of t-butyl alcohol. t-Butyl alcohol displays a tendency toward dehydration in an acidic medium and if hydrobromic

acid is present, formation of t-butyl bromide occurs. To avoid this problem, an acid chloride, 2,3-dibromopropionyl chloride was used as the intermediate in the esterification. This compound exhibits a high reactivity toward the tertiary alcohol and minimizes the side reactions associated with conventional esterification. The reaction pathway (Figure 2-7) first involved the preparation of 2,3-dibromopropionic acid from acrylic acid followed by treatment with thionyl chloride to form 2,3-dibromopropionyl chloride. t-Butyl α-bromoacrylate was then obtained directly from the acid chloride and t-butyl alcohol in the presence of quinoline.

2,3-Dibromopropionic acid[2]. In a 1 liter, 1 neck boiling flask was placed 72g (1 mole) of acrylic acid and 200 mls of diethyl ether. Cold bromine (60 mls) was added dropwise with rapid magnetic stirring. The temperature of the reaction mixture was controlled by both the rate of bromine addition and the diethyl ether solvent reflux. It was found that a solvent was necessary in this step due to the exothermic nature of the reaction. Without a solvent, localized heating resulted in large amounts of poly(acrylic acid). After allowing the reaction to stir for approximately 24 hours, the diethyl ether was distilled off and the product removed by vacuum distillation. The product, which was a white crystalline solid, had a boiling point of 110°C (1 mm). M.P.: 64-66°C; Yield: 108g (0.78 mole) of 2,3-dibromopropionic acid, 78%.

2,3-Dibromopropionyl chloride[2]. A mixture of 80g (0.35 mole) of 2,3-dibromopropionic acid was added to a 250 ml round bottom flask



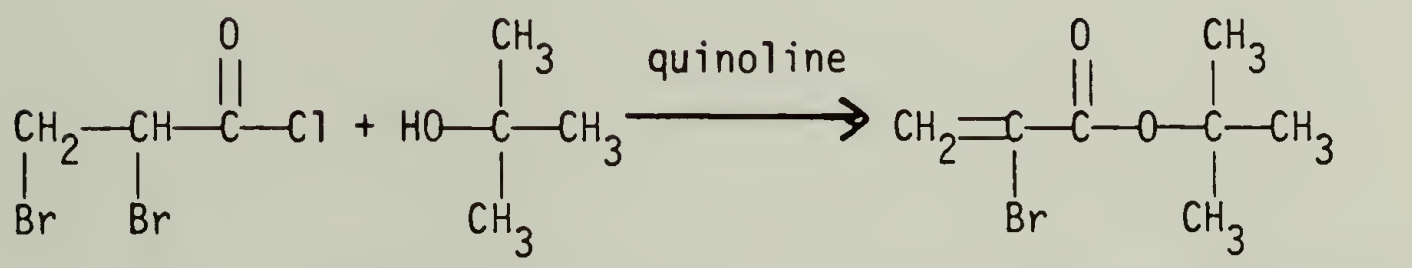


Figure 2-7. Reaction Scheme for the Synthesis of t-Butyl α-bromoacrylate

and heated gently until it dissolved. Immediately, 80g (1 mole) of thionyl chloride was added in a dropwise manner. At this point the reaction had not yet commenced since the liberation hydrochloric acid was not observed. The reaction was left overnight with continuous stirring followed by 2-3 hours of gentle reflux. Not long after beginning the reflux, the evolution of hydrochloric acid from the reaction mixture was detected. The excess thionyl chloride was removed by distillation and the product, a light yellow liquid, was removed under reduced pressure. Yield: 65g (0.24 mole) of 2,3-dibromopropionyl chloride, 71%; B.P.: 80-82°C (20 mm) [Lit[2]: 81-84°C (18 mm)].

t-Butyl α-bromoacrylate. 27g (0.1 mole) of the above 2,3-dibromopiopionyl chloride was added to a 250 ml round bottom flask containing 50 mls of dry (distilled from calcium hydride) t-butyl alcohol[9]. While employing rapid magnetic stirring, 35 mls (0.3 moles) of freshly distilled quinoline was added slowly and immediately the reaction mixture turned red and became progressively darker, almost brown, with subsequent additions. After all the quinoline had been added, the excess t-butyl alcohol was distilled from the reaction mixture followed by the final product under reduced pressure. The NMR spectra of this monomer is presented in Figure 2-8.

As with the other monomers in the series, it was collected at -78°C to prevent polymerization. Quinoline was employed for two purposes in this reaction. One was to remove hydrogen bromide as in the previous reactions and the second was to complex the by-product,

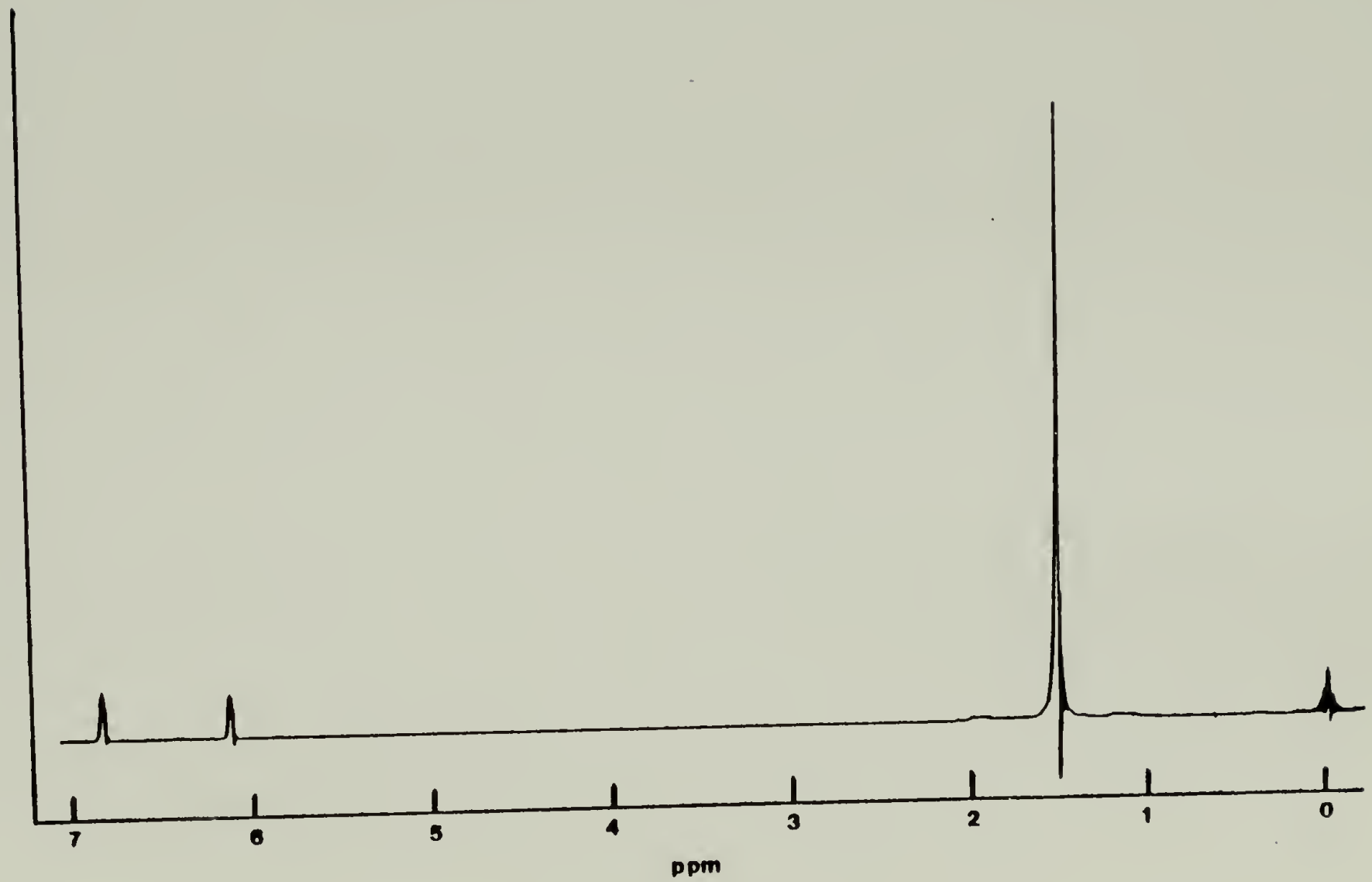


Figure 2-8. Proton NMR Spectra of t-Butyl α-bromoacrylate Recorded at 35°C in CCl_4

hydrochloric acid as it was liberated in the esterification reaction. In this way two steps were consolidated into one and thereby omitted the need for isolation of t-butyl 2,3-dibromopropionate. Although this method was suitable for the preparation of all the esters, it was not the preferred technique due to the lower overall yields and the sensitive nature of the acid chloride. Yield: 11g (0.053 mole) of t-butyl α-bromoacrylate, 53%; B.P.: 53-55°C (1 mm).

It is necessary to point out that all of the above monomers were found to undergo polymerization in the bulk state at ambient temperature. The ease of polymerizability was demonstrated by the fact that polymer formation occurred within minutes after the monomers were synthesized. This problem was alleviated by collecting the monomer at -78°C as it distilled from the reaction mixture and storing it at this temperature (crystalline state) until immediately before use. Free radical initiators such as hydroquinone were found to be ineffective in inhibiting polymerization. The methyl and ethyl esters polymerized considerably faster than the other esters such as the n-butyl and the n-pentyl. Also, the monomers turned yellow after being exposed to light for a short period of time. When they were effectively shielded from the light, they remained colorless and polymerized at a much slower rate.

Polymerization Techniques

Syndiotactic. The syndiotactic polymers were synthesized by a low temperature free radical technique in 40 to 60% volume solutions in toluene, benzene or tetrahydrofuran. Temperatures from -40 to -78°C

were employed although the majority of the experiments were performed at -40°C. Ultraviolet radiation from a low pressure mercury vapor lamp in conjunction with benzoin as a photo-initiator was employed as the source of initiation.

The experimental apparatus consisted of a Quartz reaction tube, 25 mm in diameter and 30 cm in length, immersed in a large Dewar (20 cm in diameter) containing the mercury vapor lamp and a stirring device. In addition, a cooling coil and temperature probe connected to a refrigeration unit was utilized to achieve the required temperatures. Methanol served as an excellent cooling medium because of its absence of absorption in the ultraviolet region and because it remained in the liquid state to well below -78°C. Initiator concentrations of 0.5 mole % and polymerization times of 18 hours were used in most cases. Pre-purified nitrogen was bubbled throughout the polymerizations serving as both an inert atmosphere as well as a means of agitation.

A specified amount of initiator, benzoin, was added to the reaction tube followed by addition of freshly distilled solvent. After the initiator had dissolved, the reaction vessel was immersed into the thermostatically controlled temperature bath and nitrogen was bubbled through for 30 minutes. After dropwise addition of the monomer, the nitrogen purge was continued for an additional 15 minutes after which the mercury vapor lamp switched on. The polymerization reaction was terminated by precipitating the reaction mixture into methanol followed by filtration and drying in a vacuum. The polymers were purified by precipitating them several times into methanol from chloro-form and finally drying in a vacuum for 48 hours.

Isotactic. A modified Grignard reagent consisting of the 1,4 addition product of a Grignard reagent and an unsaturated ketone, benzalacetophenone, was employed for the preparation of the isotactic polymers. Typical Grignard reagents such as methyl magnesium chloride and ethyl magnesium chloride were utilized but best results were obtained with methyl magnesium chloride. The polymerization reactions were conducted in a heptane-diethyl ether solvent mixture under purified nitrogen or high vacuum from temperatures of 35 to 55°C.

The co-catalyst, benzalacetophenone, was placed in a two necked reaction flask fitted with a reflux condenser and rubber septum followed by the addition of freshly distilled, dry, diethyl ether. After the benzalacetophenone had dissolved, dry n-heptane was distilled directly into the reaction vessel. All additions were performed in a prepurified nitrogen or argon stream. After 30 minutes of an inert gas purge the Grignard reagent, 3M in tetrahydrofuran, was added dropwise with the formation of a yellow-orange suspension which turned white after heating for 20 minutes at 90°C in a water bath. When the temperature of the reaction mixture reached the polymerization temperature (almost all of the polymerizations were conducted at 35°C) the monomer was added dropwise via syringe and the reaction vessel sealed off. Within minutes after monomer addition, a thick suspension resulting from the onset of polymerization developed. Initiator concentrations of 1 mole % were utilized for the majority of the reactions. All additions were carried out with self-sealing rubber septums and the polymerizations were shielded from light for their duration. Termination of the reactions was achieved by precipitating

the polymers with a 10% solution of hydrochloric acid in methanol. Due to the limited solubility of the isotactic polymers at room temperature, they were purified by soxhlet extraction with methanol for a period of two weeks. The procedure for preparation of the catalyst will be discussed in greater detail in Chapter III.

Atactic. A conventional free radical polymerization reaction was employed for preparation of the atactic polymers. The reactions were conducted at 50°C in toluene, benzene or tetrahydrofuran with decanoyl peroxide as the initiator. Reaction times between 18 and 36 hours and initiator concentrations of 0.1 and 1.0 mole % were utilized. All reactions were purged with purified nitrogen for a minimum of 30 minutes before and after addition of the monomer followed by sealing the vessel under a blanket of nitrogen. Precautions were exercised to exclude oxygen from inhibiting the polymerizations. The resulting polymers were dissolved, filtered and reprecipitated twice from methanol and then dried at 30°C in a vacuum for 48 hours.

Polymer Characterization

^{1}H Nuclear magnetic resonance-90 MHz. A Perkin-Elmer R-32 nuclear magnetic resonance spectrometer was used in all cases. Measurements were conducted from 35°C to 120°C using tetramethylsilane or hexamethyldisiloxane as internal standards. The polymer spectra were measured on 5-10% w/v solutions in tetrachloroethane. Quantitative determination of the tacticity for the methyl ester, methyl α-bromoacrylate, was not possible due to peak overlap between the methyl

ester resonance and backbone protons. As a result of insufficient peak separation of the ester group resonance of the higher alkyl esters, the contributions from the three triad structures could not be resolved even on a qualitative basis. The excessive overlap resulted from the very small chemical shift differences between the triad resonances relative to their coupling constants. Although the backbone $-CH_2$ proton resonance between 3.2 and 3.8 ppm could not be used as a determination of tetrad tacticity, a qualitative evaluation was possible. A quantitative measure of tacticity was possible with ^{13}C NMR spectroscopy and will be discussed further in Chapter IV.

^{13}C Nuclear magnetic resonance. A Varian CFT-20 NMR spectrometer was used for the determination of polymer tacticity. The studies were conducted in either deuterated chloroform or a mixture of tetrachloroethane and deuterated chloroform at 35°C on 10-40% w/v solutions. In general, good spectra were achieved using 10,000-50,000 transients employing a pulse width of 15 μseconds, a one second acquisition time and a delay time of 1 second. An internal deuterium lock and a tetramethylsilane reference were used in all instances.

For each sample the tacticity was measured at three different carbon atoms: the backbone methylene carbon, the quarternary carbon and the carbonyl carbon. Both the quartenary carbon and carbonyl carbon reflect pentad and triad tacticity while the backbone methylene carbon measures tetrad tacticity. The actual measurement and interpretation of the ^{13}C spectra will be discussed in detail in Chapter IV.

Infrared spectroscopy. The infrared spectra of the polymers were obtained from films solvent-cast on NaCl plates (5-10% w/v solutions) using a Perkin-Elmer model 283 infrared spectrometer. The isotactic samples were cast from tetrachloroethane while chloroform was used for all others. All polymers but the methyl ester showed a weak correlation with tacticity for the C-H stretching absorptions between 1350 and 1470 cm^{-1} [8].

Molecular weight. The molecular weights and molecular weight distributions were determined in tetrahydrofuran solutions using a Waters gel permeation chromatograph model 501. Concentrations of 0.1 to 0.3% w/v were employed for all measurements. The molecular weight calibration curve was determined with narrow molecular weight polystyrene standards under identical conditions.

Elemental analysis. The elemental analysis of the compounds prepared in this investigation were carried out by the Microanalytical Laboratory of the University of Massachusetts.

Differential scanning calorimetry. Measurements were conducted on a Perkin-Elmer differential scanning calorimeter, 2-B, using 5-20 mg samples and scanning rates from 20-80°C/minute. Crystalline melting points and glass transition temperatures were not measurable because of the low thermal stability of the polymers. Even slight heating resulted in the formation of lactone rings along the polymer backbone making quantitative thermal measurements impossible.

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C H A P T E R I I I

THE CHARACTERIZATION OF POLY(ALKYL α-BROMOACRYLATE)S OF VARIED STEREOCHEMICAL STRUCTURE

Introduction

A series of six alkyl α-bromoacrylate esters have been polymerized into a wide range of stereo-chemical structures utilizing three different polymerization techniques. Specifically, isotactic polymers were synthesized using a modified Grignard complex consisting of the reaction product between a Grignard reagent and benazlacetophenone while a low temperature, photolytically induced, free radical polymerization reaction was employed for the preparation of the corresponding syndiotactic polymers. Polymers of intermediate tacticity, i.e., atactic, were prepared by a conventional free radical polymerization reaction at 50°C, utilizing decanoyl peroxide as the initiator. The polymerizations were conducted with the methyl, ethyl, n-propyl, i-propyl, n-butyl, and n-pentyl α-bromoacrylates. Only atactic poly(t-butyl α-bromoacrylate) was synthesized due to its failure to polymerize either with the modified Grignard complex or at temperatures below -20°C.

The principal motivation behind this investigation was to synthesize a series of high molecular weight, highly stereoregular poly(alkyl α-bromoacrylate)s where the influence of the steric structure on the glass transition temperature could be evaluated. Correlation of the available glass transition temperature data for monosubstituted vinyl polymers, $\{CH_2\ CHR\}_n$, and α,α-disubstituted vinyl polymers,

$\{CH_2CR_1R_2\}_n$, led Karasz, Bair and O'Reilly[1] to the conclusion that the steric configuration had a major effect on the glass transition temperature only in the disubstituted case. The poly(alkyl methacrylate) series, which has been studied extensively, exhibits this trend exceptionally well[2].

This empirical observation was explained by Karasz and MacKnight[3] who interpreted the phenomena by employing the Gibbs-DiMarzio glass transition theory as a foundation[4]. The assumption was made that effect of tacticity on the glass transition temperature was intramolecular in nature and independent of intermolecular effects caused by changes in pendant ester group size[3]. This treatment resulted in an expression relating the differences in the glass transition temperature for an isotactic-syndiotactic pair of any poly(alkyl methacrylate). Realizing the similarity in size (van der Waals radius) between a methyl group and chlorine atom, Karasz and MacKnight postulated that the glass transition differences between a syndiotactic and isotactic pair of the poly(alkyl α-chloroacrylate)s should be of a similar magnitude.

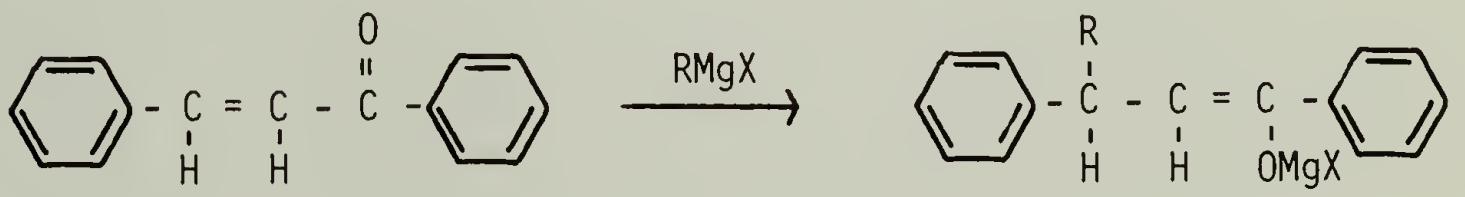
An investigation from this laboratory[5] concerning stereoregular poly(alkyl α-chloroacrylate)s revealed glass transition temperature differences somewhat lower than predicted by the theory. This was attributed, at least in part, to the intermolecular forces arising from the polar chlorine atom. Thus, the poly(alkyl α-bromoacrylate) series was the next choice because of the lower degree of polarity associated with the bromine atom as compared to the chlorine.

During the course of this investigation, the alkyl α-bromoacrylate polymers were found to undergo an internal cyclization reaction

producing butyrolactone groups along the polymer backbone. The formation of this five membered lactone occurred at temperatures as low as 60°C for all the polymers and therefore made the evaluation of their glass transition temperatures impossible. The effects of polymer tacticity on degree of lactone formation will be investigated in detail in Chapter V of this dissertation.

Modified Grignard Complex-Isotactic Polymers

The first highly isotactic, crystallizable poly(methyl α-chloroacrylate) of high molecular weight was synthesized by Breslow and Kutner[6] by means of a modified Grignard complex. Although numerous other techniques have been tried, none have come close to duplicating this result[5,7-10]. The complex, an addition product of a Grignard reagent to an α,β-unsaturated ketone such as benzalacetophenone, was presumed to have the following structure[6];



where RMgX represents the Grignard reagent. Typical Grignards found to be effective were: ethyl magnesium chloride, isopropyl magnesium chloride and ethyl magnesium bromide while catalyst activity was also observed with other α,β-unsaturated ketones like benzalacetone. It was stated[6] that the polymerizations could be conducted from -30 to 68°C

with no change in polymer stereoregularity although NMR spectra were not offered as proof. In addition, excess benzalacetophenone decreased the catalyst efficiency but increased its stereospecificity. On the other hand, an excess of the Grignard produced the desired catalyst complex as well as a mixture of other species which were less effective in producing isotactic structures.

The catalyst structure proposed by Breslow and Kutner was substantiated by Uryu, Okaku and Matsuzaki[7] by reacting benzalacetophenone with ethyl magnesium chloride and phenyl magnesium chloride under the identical conditions used for catalyst preparation. After the reaction products were hydrolyzed with hydrochloric acid and purified, the melting points and infrared and NMR spectra confirmed the structures to be phenyl β-phenylbutyl ketone and phenyl β,β-diphenylethyl ketone, respectively. These compounds corresponded to the hydrolysis products of the catalyst species suggested by Breslow and Kutner.

An investigation concerning the effect of α,β-unsaturated ketones on the preparation of isotactic poly(ethyl α-chloroacrylate), revealed compounds such as: dibenzylacetone, benzalacetone, mesityl oxide and methyl vinyl ketone to be nearly as effective as benzalacetophenone[7]. Of all the ketones tried, benzalacetophenone produced the highest degree of isotactic units, 87% on a triad basis. Propiophenone and propylene oxide displayed no stereospecific activity and produced only atactic polymers. The catalyst structure prepared with ethyl magnesium chloride and propiophenone or propylene oxide should both have had partial structures of -C-C-OMgCl. On the other hand, all of the effective catalyst complexes should have had structures containing a vinyl group

adjacent to the carbon-oxygen bond, -C-C-O-MgCl. Thus, it seems reasonable to assume that the double bond exerted a controlling influence on the mechanism involved in isotactic placement. Apparently the stereoregulating power of the catalyst complex required the presence of both a carbon-carbon double bond and an oxygen-magnesium bond.

Dever and co-workers[5] successfully synthesized isotactic polymers of the methyl, ethyl and i-propyl α-chloroacrylates with this polymerization catalyst. Triad tacticities of 68, 61 and 51% were achieved for the three esters, respectively. Ethyl magnesium chloride and benzalacetophenone were employed as the catalyst combination in all cases.

All of the polymerizations in the present investigation were conducted with benzalacetophenone as the unsaturated ketone and almost exclusively with methyl magnesium chloride as the Grignard reagent. Tables 3-1 through 3-7 list the experimental conditions utilized in the preparation of all the polymers. Ethyl magnesium chloride was used in the polymerization of both methyl α-bromoacrylate, experiment 1, and ethyl α-bromoacrylate, experiment 2, but the yields were considerably lower than those from methyl magnesium chloride and therefore, its use was discontinued. Quantitative measurements of tacticity were not carried out with the polymers prepared from ethyl magnesium chloride but qualitatively appeared to be less isotactic.

During the course of the experiments, it was discovered that the concentration of diethyl ether had a significant effect on the yield of the polymerization reactions. When only small amounts of diethyl ether were present (<5%) the yields were always below 10% while with

Table 3-1. Reaction Conditions for Synthesis of the Poly(methyl α-bromoacrylate)s.

Sample	Initiator(I)	% I	Solvent[a]	T(°C)	t(hr.)	Yield	M_n
1	Modified Grignard[b]	2	Heptane-Ether	35	15	4	3,500
2	Modified Grignard[c]	2	Heptane-Ether	55	15	10	3,000
3	Modified Grignard[d]	1	Heptane-Ether	35	18	8	31,000
4	Decanoyl Peroxide	1	Toluene	50	42	49	33,000
5	Decanoyl Peroxide	0.1	Toluene	50	42	18	28,000
6	Decanoyl Peroxide	0.1	Benzene	50	42	11	24,500
7	Decanoyl Peroxide	0.1	THF	50	42	10	31,500
8	Benzoin	0.5	Toluene	-40	18	9	29,500
9	Benzoin	1	THF	-78	20	1	26,000
10	None	0	None	35	30 days	90	13,000

a. 50 volume % monomer
b. 2 times excess Ethyl magnesium chloride
c. 2 times excess Methyl magnesium chloride
d. slight excess Benzalacetophenone

Table 3-2. Reaction Conditions for Synthesis of the Poly(ethyl α-bromoacrylate)s

Sample	Initiator(I)	% I	Solvent[a]	T(°C)	t(hr.)	Yield	M_n
11	Modified Grignard[b]	2	Heptane-Ether	35	18	14	12,000
12	Modified Grignard[c]	2	Heptane-Ether	35	18	20	14,500
13	Modified Grignard[d]	2	Heptane-Ether	35	18	8	9,000
14	Modified Grignard[e]	1	Heptane-Ether	35	18	15	37,000
15	Modified Grignard[c]	1	Heptane	35	18	7	6,500
16	Decanoyl Peroxide	1	Toluene	50	42	56	21,000
17	Decanoyl Peroxide	0.1	Toluene	50	42	10	40,000
18	Benzoin	1	THF	-78	18	0	-
19	Benzoin	1	Toluene	-78	18	0	-
20	Benzoin	1	Toluene	-50	18	3	38,500
21	Benzoin	0.5	Toluene	-45	18	5	37,000
22	Benzoin	0.5	Toluene	-40	18	7	42,000

a. 50 volume % monomer
b. 1.25 times excess Ethyl magnesium chloride
c. 1.25 times excess Methyl magnesium chloride
d. 2 times excess Methyl magnesium chloride
e. slight excess Benzalacetophenone

Table 3-3. Reaction Conditions for Synthesis of the Poly(n-propyl α-bromoacrylate)s

Sample	Initiator(I)	% I	Solvent[a]	T(°C)	t(hr.)	Yield	M_n
23	Modified Grignard[b]	1	Heptane-Ether	35	18	33	34,500
24	Decanoyl Peroxide	1	Toluene	50	24	46	8,000
25	Decanoyl Peroxide	0.1	Toluene	50	24	5	14,500
26	Decanoyl Peroxide	1	Toluene	60	15	46	6,500
27	Benzoin	1	THF	-78	24	0	-
28	Benzoin	1	Dichloromethane	-78	24	0	-
29	Benzoin	0.5	Toluene	-78	24	0	-
30	Benzoin	0.5	Toluene	-40	18	7	44,000

a. 50 volume % monomer
b. slight excess Benzalacetophenone

Table 3-4. Reaction Conditions for Synthesis of the Poly(i-propyl α-bromoacrylate)s

Sample	Initiator(I)	% I	Solvent[a]	T(°C)	t(hr.)	Yield	M_n
31	Modified Grignard[b]	1	Heptane-Ether	35	20	7	90,000
32	Decanoyl Peroxide	1	Toluene	50	42	15	26,000
33	Decanoyl Peroxide	0.1	Toluene	50	24	3	35,500
34	Decanoyl Peroxide	1	Toluene	60	12	28	19,000
35	Benzoin	1	Toluene	-78	18	0	-
36	Benzoin	0.5	Toluene	-40	18	4	45,000
37	Decanoyl Peroxide	0.1	Bulk	50	24	0	-

a. 50 volume % monomer
b. slight excess Benzalacetophenone

Table 3-5. Reaction Conditions for Synthesis of the Poly(n-butyl α-bromoacrylate)s

Sample	Initiator(I)	% I	Solvent[a]	T(°C)	t(hr.)	Yield	M_n
38	Modified Grignard[b]	1	Heptane	35	20	2	19,000
39	Modified Grignard[c]	1	Heptane-Ether	35	15	18	93,500
40	Decanoyl Peroxide	1	Toluene	50	42	51	25,500
41	Decanoyl Peroxide	0.1	Toluene	50	24	5	20,500
42	Benzoin	1	Toluene	-78	18	0	-
43	Benzoin	0.5	Toluene	-40	18	2	48,000

a. 50 volume % monomer
b. 2 times excess Methyl magnesium chloride
c. slight excess Benzalacetophenone

Table 3-6. Reaction Conditions for Synthesis of the Poly(n-pentyl α-bromoacrylate)s

Sample	Initiator(I)	% I	Solvent[a]	T(°C)	t(hr.)	Yield	M_n
44	Modified Grignard[b]	1	Heptane-Ether	35	20	16	89,000
45	Decanoyl Peroxide	1	Toluene	50	42	29	33,000
46	Decanoyl Peroxide	0.1	Toluene	50	24	9	44,000
47	Benzoin	0.5	Toluene	-40	18	1	63,000
48	Decanoyl Peroxide	0.1	Bulk	50	18	1	16,000

a. 50 volume % monomer
b. slight excess Benzalacetophenone

Table 3-7. Reaction Conditions for Synthesis of the Poly(t-butyl α-bromoacrylate)

Sample	Initiator(I)	% I	Solvent[a]	T(°C)	t(hr.)	Yield	M_n
49	Modified Grignard[b]	1	Heptane-Ether	35	18	0	-
50	Modified Grignard[b]	2	Heptane-Ether	35	18	0	-
51	Decanoyl Peroxide	1	Toluene	50	18	0	-
52	Decanoyl Peroxide	2	Toluene	50	24	0	-
53	Decanoyl Peroxide	0.5	None	50	24	40	208,000
54	Benzoin	1	Toluene	-20	15	0	-

a. 50 volume % monomer
b. slight excess Benzalacetophenone

ether concentrations of 10 to 20% the yields were generally in excess of 30%. In addition, it was found that if ether was totally absent from the system, the resulting polymer was severely deficient in bromine content, usually by 10 to 15%. Evidently, the ability of diethyl ether to function as a complexing agent prevented the abstraction of bromine by either the initiating or propagation species. The bromine content of the polymers were very close to the theoretical as long as ether was present in excess of about 2 volume %. Breslow and Kutner[6] briefly suggested the need for a complexing agent such as diethyl ether but stated nothing further.

The need for an exact one-to-one ratio between the two co-catalysts was pointed out by Breslow and Kutner[6] and later by Dever and co-workers[5]. In the latter case, evidence was observed for a two state propagation mechanism when the Grignard reagent was present in an excess. The polymers could be fractionated into two portions, one composed of highly isotactic units and the other composed of atactic units. For instance, unfactionated poly(ethyl α-chloroacrylate) contained 65% isotactic triads but after fractionation a portion containing 81% isotactic units was isolated. A sample of poly(i-propyl α-bromoacrylate) which was composed of 51% isotactic units was found to contain two fractions of roughly equal size after fractionation where one of the fractions had an isotactic content of 90%. The Grignard reagent itself must have been responsible for the production of the atactic repeat units and clearly was not able to exert any stereo-control on monomer addition and as a result, only atactic units were propagated.

With this in mind, the stereoregular polymerizations were conducted employing several different ratios of the two co-catalysts in order to determine the effects of an excess of either co-catalyst on the tacticity and molecular weight. Tables 3-1 and 2 show the different co-catalyst ratios and polymerization conditions for poly(methyl α-bromoacrylate) and poly(ethyl α-bromoacrylate), respectively. Samples 2 and 13 were synthesized with a two-fold excess of methyl magnesium chloride and displayed exceptionally large molecular weight distributions, 11.6 for the methyl ester and 7.9 for the ethyl ester, as shown in Table 3-8. The molecular weight curves (from gel permeation chromatography) were resolved into two peaks, one of relatively high molecular weight and one of very low molecular weight. This was evidence for a two-state model where the high molecular weight peak was produced from the expected Grignard complex polymerization and the low molecular weight contribution resulted from the unwanted Grignard polymerization. The low molecular weight peaks in each sample were typical of previous results with the poly(alkyl α-chloroacrylate)s initiated by Grignard reagents[5,9,10].

As a result of this finding, a substantial amount of effort was spent in perfecting the conditions for catalyst preparation. The most effective ratio was, of course, 1 to 1 but was exceedingly difficult to achieve due to the difficulty involved in measuring the exact concentration of the Grignard reagent. The method of Gilman[7], involving the titration of the Grignard with acid, was utilized to determine the molarity of the Grignard solutions but a significant amount of error still resulted from high reactivity of the Grignard to almost any

Table 3-8. The Effect of Excess Methyl Magnesium Chloride on the Molecular Weight and Molecular Weight Distribution in the Synthesis of Poly(methyl α-bromoacrylate) and Poly(ethyl α-bromoacrylate)

Sample	Ester	Peak	M_n	M_w	M_w/M_n
2[a]	Methyl	Total	3,000	33,500	11.6
2[a]	Methyl	A	21,500	57,000	2.68
2[a]	Methyl	B	1,500	3,000	2.33
3[b]	Methyl	Total	31,000	105,000	3.35
13[a]	Ethyl	Total	9,000	70,000	7.89
13[a]	Ethyl	A	31,500	87,000	2.77
13[a]	Ethyl	B	2,500	4,000	1.72
14[b]	Ethyl	Total	37,000	114,500	3.09

a. 2-fold excess Methyl magnesium chloride
b. slight excess Benzalacetophenone

foreign substances, including air. In addition, the difficulty in measuring the small quantities used in the polymerizations and the ease with which the Grignard precipitated out of solution compounded the error.

Accordingly, a technique was developed to achieve a stoichiometric equivalence between the two co-catalysts, regardless of the concentration and quantities involved. The following is a description of the procedure and for the sake of convenience, the preparation of 1 mole of catalyst will be considered. To the reaction vessel containing the solvent, n-heptane and diethyl ether (20%) was added 0.75 moles benzalacetophenone (a yellow solution), 0.25 M in ether, followed by the dropwise addition of 0.25 moles methyl magnesium chloride, 3M in tetrahydrofuran, with rapid stirring. The mixture, now an orange suspension, was transformed into a white precipitate after heating for 15 minutes at 90°C. The remainder of the Grignard reagent, 0.75 moles, was added in 0.25 mole portions followed by heating each time as before. At this point the reaction mixture consisted of a white fluffy precipitate in a clear, colorless solvent. The colorless solvent indicated either an exact 1 to 1 ratio between the co-catalysts or an excess of the Grignard reagent which should be the case here. The 0.25 M benzalacetophenone solution was added dropwise until the orange color no longer developed and then was heated for a final 20 minutes. Now, the solvent showed a slight yellow tint and indicated a slight excess of benzalacetophene, probably about 0.1 times. After the reaction vessel was brought to the polymerization temperature, the monomer was added as described in the experimental section.

Several experiments were conducted to isolate the white catalyst complex from the medium from which it was prepared. It was hoped that if the excess benzalacetophenone could be removed under anhydrous conditions, the catalyst activity could be increased. Thus, the catalyst was prepared as usual, vacuum filtered from the reaction solution, washed several times with dry diethyl ether and then replaced into a reaction vessel containing fresh n-heptane and diethyl ether. The subsequent addition of monomer revealed that the catalyst complex was no longer an active species and was unable to initiate polymerization. The reason for this was not clear, however, it may be that the active catalyst required the presence of other species in the reaction mixture which were removed upon filtration. No further investigations along this direction were conducted.

The preceding technique for catalyst preparation was employed for all of the modified Grignard polymerizations where an excess of benzalacetophenone was used (Tables 3-1 through 3-6 and 3-8). The molecular weights were invariably higher in those cases and unquestionably resulted from the equivalence between the two co-catalysts. The molecular weight curves were unimodal and displayed distributions close to 3.0. The molecular weights and molecular weight distributions will be discussed in greater detail in a subsequent section of this chapter.

Further evidence for the achievement of an exact 1 to 1 correspondence between the Grignard reagent and benzalacetophenone can be seen in Table 3-9 where the triad tacticities for these polymerizations are listed. These triad tacticities were calculated from the pentad

Table 3-9. Triad Tacticities Calculated from the Pentad Tacticity of the Carbonyl Carbon Resonance for the Polymers Synthesized with the Modified Grignard Complex

Ester	Sample	A/B	% Triads		
			Isotactic	Atactic	Syndiotactic
Methyl[a]	2	2	0.28	0.39	0.33
Methyl	3	1	0.68	0.26	0.06
Ethyl[b]	13	2	0.32	0.40	0.28
Ethyl	14	1	0.66	0.27	0.07
n-Propyl	23	1	0.74	0.21	0.05
i-Propyl	31	1	0.60	0.30	0.10
n-Butyl	39	1	0.64	0.29	0.07
n-Pentyl	44	1	0.70	0.25	0.05

A = Methyl magnesium chloride, B = Benzalacetophenone

a. from Methyl ester resonance in ^{1}H NMR spectroscopy
b. calculated from backbone methylene resonance

tacticity of the carbonyl carbon resonance determined by ^{13}C NMR spectroscopy (Chapter IV). Immediately obvious was the drastic increase in the isotactic content as the methyl magnesium chloride to benzalacetophenone ratio decreased. This phenomenon presented further evidence for the need of a 1 to 1 ratio between the two co-catalysts. In the cases where this ratio (A/B) was equal to one or slightly less, the isotactic triad values were fairly consistent and ranged from 0.60 to 0.74. The polymers of low isotactic content were fractionated into samples of higher and lower stereoregularity but the tacticity of the highly isotactic polymers were not significantly improved by this technique.

Free Radical Polymerization

Preparation of syndiotactic polymers. Predominately syndiotactic polymers can be synthesized at low temperatures because of the difference in activation energies associated with isotactic and syndiotactic placement[12]. The formation of a syndiotactic repeat unit requires slightly less activation energy than the formation of the corresponding isotactic unit due to a lesser degree steric repulsion in the syndiotactic configuration. Therefore, a decrease in the polymerization temperature will produce more syndiotactic units relative to isotactic units. At a sufficiently low temperature, such as -78°C, polymers containing close to 80% syndiotactic units can be prepared[8,9].

Several different polymerization solvents including: toluene, methylene chloride and tetrahydrofuran were utilized but best yields were achieved with toluene because of better initiator and polymer

solubility at the low temperatures employed in the polymerization reactions. Only the methyl ester polymerized at -78°C and in fact, the only other monomer that polymerized below -50°C was ethyl α-bromoacrylate (Table 3-2). At -40°C, only t-butyl α-bromoacrylate would not polymerize and even at -20°C polymer formation was not possible.

The polymer yields decreased as the polymerization temperature decreased and as the ester group size increased. For instance, at -40°C the yields decreased from 9.0 to 1.0% for the methyl through the n-pentyl esters. This trend was a consequence of steric effects which became increasingly important as the size of the ester group increased. The failure of t-butyl α-bromoacrylate to polymerize, even at -20°C, further substantiated this rationale.

The effect of temperature was demonstrated by ethyl α-bromoacrylate where polymerizations conducted at -40, -45 and -50°C resulted in yields of 7.0, 5.0 and 3.0 (Table 3-2). As the reaction temperature decreased, the rate of polymerization also decreased and at low enough temperatures insufficient energy was available to continue the propagation mechanism. Since the initiator radicals were generated as a result of ultraviolet radiation, the process was fairly temperature independent and the radicals were generated regardless of the reaction temperature.

The tacticities for the samples polymerized at -40°C ranged between 0.60 and 0.66 syndiotactic triads, as shown in Table 3-10. The fraction of syndiotactic triads for poly(methyl α-bromoacrylate) was seen to increase from 0.66 to 0.77 with a decrease in the polymerization temperature from -40 to -78°C. This was consistent with the fact that a syndiotactic placement had a slightly lower energy of activation

Table 3-10. Triad Tacticities Calculated from the Pentad Tacticity of the Carbonyl Carbon Resonance for the Polymers Synthesized with the Benzoin and Ultraviolet Light.

Ester	Sample	Polymerization Temp.°C	% Triads		
			Isotactic	Atactic	Syndiotactic
Methyl	8	-40	0.03	0.31	0.66
Methyl[a]	9	-78	0.01	0.22	0.77
Ethyl	22	-40	0.03	0.33	0.64
n-Propyl	30	-40	0.04	0.34	0.62
i-Propyl	36	-40	0.05	0.35	0.60
n-Butyl	43	-40	0.04	0.35	0.61
n-Pentyl	47	-40	0.03	0.33	0.64

a. from Methyl ester resonance in ^{1}H NMR spectroscopy

associated with it, as was previously mentioned. The tacticities for all the samples prepared at -40°C were in close proximity to each other for obvious reasons. A further discussion on the effect of polymerization temperature on tacticity will be presented in Chapter IV.

Preparation of atactic polymers. The atactic polymers were prepared at 50°C employing a conventional free radical polymerization. Initially, the polymerization reactions were conducted at 60°C, but the temperature was found to be excessive due to the thermal instability of the polymers. This will be discussed in detail in Chapter V. Decanoyl peroxide was utilized as the free radical initiator since it had a half life of 12 hours at 50°C[13]. Both azobisisobutyronitrile and benzoyl peroxide have considerably longer half lives at this temperature and longer polymerization times would be required to achieve an appreciable quantity of initiating radicals.

Table 3-11 lists the triad tacticities of the polymers polymerized with 1% decancoyl peroxide at 50°C. The values were very typical of atactic polymers in general. Comparison of Tables 3-10 and 3-11 revealed that as the temperature was increased from -40 to 50°C, the percentage of isotactic units in the polymers rose significantly and conceivably, at a high enough temperature, a purely heterotactic polymer could have been synthesized[14]. At this temperature there would be sufficient energy in the system to produce isotactic or syndiotactic placements with equal frequency, regardless of the activation energies associated with each configuration. The effects of the polymerization mechanism on the polymer tacticity will be discussed in detail in Chapter IV.

Table 3-11. Triad Tacticities Calculated from the Pentad Tacticity of the Carbonyl Carbon Resonance for the Polymers Synthesized with 1% Decanoyl Peroxide

Ester	Sample	Polymerization Temp °C	% Triads		
			Isotactic	Atactic	Syndiotactic
Methyl	4	50	0.10	0.44	0.46
Ethyl	16	50	0.11	0.46	0.43
n-Propyl	24	50	0.09	0.47	0.44
i-Propyl	32	50	0.11	0.43	0.46
n-Butyl	40	50	0.09	0.46	0.45
n-Pentyl	45	50	0.10	0.44	0.46

The preparation of poly(t-butyl α-bromoacrylate) was achieved only in bulk at 50°C. The reactions conducted in solution, including those at -40°C and with the modified Grignard complex, failed to produce polymers. A similar behavior was observed with the other α-bromoacrylate monomers where it was found that they would polymerize in their pure state at room temperature in the absence of any initiator, but would not polymerize if any solvent was present. This phenomenon was observed in solvents such as: toluene, benzene, tetrahydrofuran or chloroform. Clearly, some type of solvent interaction was responsible for retarding or totally inhibiting the polymerization reaction, although the exact nature of the interaction was not known. It is conceivable for the monomers to polymerize by anionic means since hydroquinone was found to be ineffective in preventing polymerization, particularly at elevated temperatures.

Molecular Weights and Molecular Weight Distributions

The polymers synthesized by the modified Grignard reagent had relatively narrow molecular weight distributions as compared to typical Grignard initiated polymerizations (Table 3-12). For instance, Goode and co-workers[15,16] reported that phenyl magnesium bromide at 0°C gave isotactic poly(methyl methacrylate) with a very broad distribution, Mw/Mn = 23.6. Polymerizations initiated by other Grignards[17-19], as well as a wide variety of organolithium compounds[17,20-22] have resulted in similar broad distributions. Breslow and Kutner[6] stated that the molecular weight distribution of poly(methyl methacrylate) synthesized

Table 3-12. Molecular Weights and Molecular Weight Distributions for Polymers Synthesized with the Modified Grignard Reagent

Ester[a]	Sample	M_n	M_w	M_w/M_n
Methyl	3	31,000	105,000	3.35
Ethyl	14	37,000	114,500	3.09
n-Propyl	23	34,500	108,000	3.12
i-Propyl	31	90,000	291,500	3.24
n-Butyl	39	93,500	280,000	2.99
n-Pentyl	44	89,000	283,000	3.18

a. all polymers synthesized with a slight excess Benzalacetophenone.

by the complex Grignard reagent was in the vicinity of 2 but no mention was made of the distribution for poly(methyl α-chloroacrylate).

All of the polymers synthesized by the modified Grignard complex in this investigation had distributions very close to one another, ranging from 2.99 to 3.35, which was an indication of a consistent catalyst preparation, i.e., a consistent ratio between the two co-catalysts. Presumably, polymer fractionation could have lead to a further decrease in the distribution, although values below 2 would probably be very difficult to achieve. No other molecular weight studies of modified Grignard polymerizations have been reported, but it is evident that this initiating system is capable of producing highly stereoregular polymers of a relatively narrow molecular weight distribution.

The narrowest polydispersities, from 1.63 to 2.17, were achieved with the low temperature free radical polymerizations, Table 3-13. This was attributed to the low polymerization temperature where chain transfer reactions were minimized. The effect of chain transfer reactions was further demonstrated by the free radical polymerizations at 50°C where the molecular weight distributions were considerably broader.

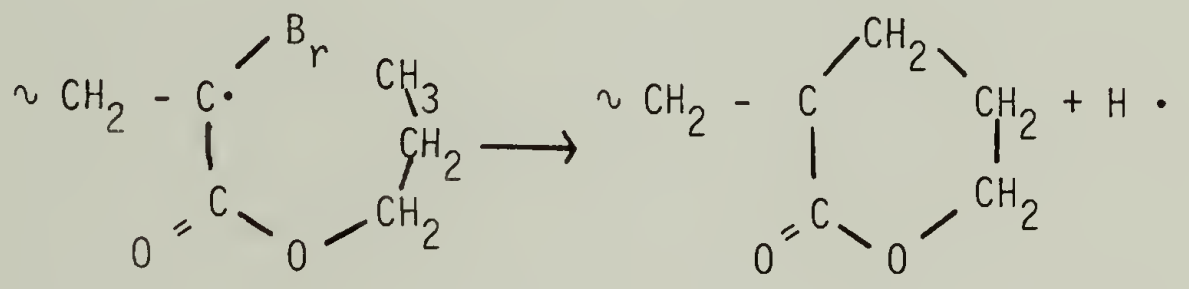
It was somewhat surprising that the number average molecular weights of all poly(methyl α-bromoacrylate)s were between 26,000 and 33,000 regardless of the polymerization technique or temperature. In addition, the highest number average molecular weight was obtained with the poly(n-pentyl α-bromoacrylate) at -40°C. Perhaps the chain transfer

Table 3-13. Molecular Weights and Molecular Weight Distributions for Polymers Synthesized with Benzoin at -40°C

Ester	Sample	M_n	M_w	M_w/M_n
Methyl	8	29,500	62,000	2.10
Ethyl	22	42,000	92,000	2.17
n-Propyl	30	44,000	94,500	2.15
i-Propyl	36	45,000	75,000	1.63
n-Butyl	43	48,000	89,000	1.84
n-Pentyl	47	63,000	128,000	2.04

or termination reactions inherent in the polymerizations placed an upper limit on the conversion to polymer.

The n-propyl ester displayed the lowest molecular weight of all the polymers prepared at 50°C with either a 0.1 or 1% initiator concentration, Table 3-14. A backbiting reaction involving the n-propyl ester group forming a terminal six-membered lactone ring could account for a low molecular weight polymer. The thermodynamic stability of the



six-membered ring would be the driving force for the reaction. The fact that low molecular weight poly(n-propyl α-bromoacrylate) was not observed at -40°C signified that the proton abstraction reaction required more activation energy than was available at this low temperature. Furthermore, this reaction would not be expected to occur in the modified Grignard polymerization and indeed this was reflected by the relatively high molecular weight produced by this technique. On the other hand, it is surprising that evidence for this chain transfer reaction was not seen with poly(ethyl α-bromoacrylate) where a five-membered lactone would result, also a favorable structure.

t-Butyl α-bromoacrylate would only polymerize in bulk, i.e., no solvent, and its molecular weight was the highest of all samples in this

Table 3-14. Molecular Weights and Molecular Weight Distributions for Polymers Synthesized with Decanoyl Peroxide at 50°C.

Ester	Sample	% Initiator	M_n	M_w	M_w/M_n
Methyl	5	0.1	28,000	84,000	3.01
Ethyl	17	0.1	40,000	128,500	3.20
n-Propyl	25	0.1	14,000	25,000	1.73
i-Propyl	33	0.1	35,500	109,000	3.07
n-Butyl	41	0.1	20,500	59,500	2.89
n-Pentyl	46	0.1	44,000	138,000	3.12
Methyl	4	1.0	33,000	69,500	2.12
Ethyl	16	1.0	21,000	53,500	2.58
n-Propyl	24	1.0	8,000	27,000	3.44
i-Propyl	32	1.0	26,000	65,000	2.46
n-Butyl	40	1.0	25,500	66,500	2.61
n-Pentyl	45	1.0	33,000	98,500	2.96
t-Butyl (bulk)	53	0.5	208,000	472,000	2.27

investigation. The reason for this was not clear but may be due to the absence of solvent interactions which can significantly reduce the rate of polymerization.

Elemental Analysis

The polymers synthesized by the modified Grignard complex with a slight excess of benzalacetophenone contained very close to the theoretical amount of carbon, hydrogen and bromine as shown in Table 3-15. The bromine contents were never deficient by more than 1%, in accordance with the results of Dever and co-workers on the poly(alkyl α-chloroacrylate)s[5]. In cases where the Grignard reagent was used in excess, the bromine loss was somewhat higher, usually around 2 or 3%. This was in agreement with other researchers[5,10] who found similar chlorine deficiencies for the poly(alkyl α-chloroacrylate)s initiated by Grignard reagents.

The polymerizations conducted at 50°C resulted in polymers deficient by 1 to 2% except for the i-propyl ester which was nearly 3% below the theoretical amount. At elevated temperatures the poly(alkyl α-bromoacrylate)s were found to undergo an internal cyclization reaction forming five-membered lactone groups along the polymer backbone. The reaction was accompanied by the loss of the appropriate alkyl bromide, i.e., the loss of methyl bromide for poly(methyl α-bromoacrylate). Evidently, this reaction was facile even at 50°C for the i-propyl ester. This observation was in agreement with the results presented in Chapter V where poly(i-propyl α-bromoacrylate) exhibited the highest reactivity towards lactone formation of all the esters except the t-butyl.

Table 3-15. Results of Elemental Analysis for Seven Poly(alkyl α-bromoacrylate) Esters.

A. Isotactic[a]

Element	Methyl	Ethyl	n-Propyl	i-Propyl	n-Butyl	n-Pentyl	t-Butyl[b]
C	30.14	34.30	38.48	37.93	40.52	44.01	-
H	3.32	4.33	5.05	4.80	5.09	6.56	-
Br	47.48	43.81	40.80	41.02	38.77	36.20	-

B. Syndiotactic[c]

C	30.15	33.81	38.58	37.32	39.98	44.04	-
H	3.12	3.89	5.13	5.14	5.42	6.62	-
Br	48.57	44.01	41.34	42.54	40.88	37.08	-

C. Atactic[d]

C	29.35	34.87	37.16	38.28	40.13	43.93	40.05
H	2.98	4.32	4.73	4.71	5.29	6.02	5.42
Br	48.59	42.42	40.81	38.48	37.66	34.20	37.82

D. Theoretical

C	29.12	33.54	37.33	37.33	40.60	43.46	40.60
H	3.05	3.94	4.70	4.70	5.35	5.92	5.35
Br	48.43	44.64	41.39	41.39	38.59	36.14	38.59

a. slight excess Benzalacetophenone
b. polymerization conducted in bulk
c. polymerized with Benzoin at -40°C
d. polymerized with 1% Decanoyl Peroxide

All of the polymers synthesized at low temperatures contained the theoretical amounts of carbon, hydrogen and bromine. The theoretical bromine content indicated that lactone formation was not possible at the low temperatures employed in the polymerizations.

^{1}H NMR Spectroscopy - 90 mHz

The 90 mHz nuclear magnetic resonance spectra for the isotactic and syndiotactic poly(alkyl α-bromoacrylate)s are given in Figures 3-1 through 3-6 and in Figure 3-7 for atactic poly(t-butyl α-bromoacrylate). Quantitative determination of tacticity was not possible for any of the polymers in this investigation although qualitative information was possible from the backbone methylene protons between 3.1 and 3.8 ppm downfield from tetramethylsilane (TMS).

The polymers prepared by the modified Grignard complex exhibited near perfect AB quartets for the backbone protons which indicated a high degree of isotacticity. A 100% isotactic polymer should theoretically display only a perfect quartet while the corresponding syndiotactic polymer would exhibit one sharp singlet. The shape of the peaks from the backbone protons revealed that the isotactic polymers were highly stereoregular and probably more so than the syndiotactic polymers prepared at -40°C. Comparison of Tables 3-9 and 3-10 for the triad tacticity of these polymers confirmed this qualitative observation. Thus, the resemblance of a quartet indicated an isotactic character, a singlet represented syndiotactic character and an unsymmetrical multiplet signified something of intermediate tacticity. Dever and

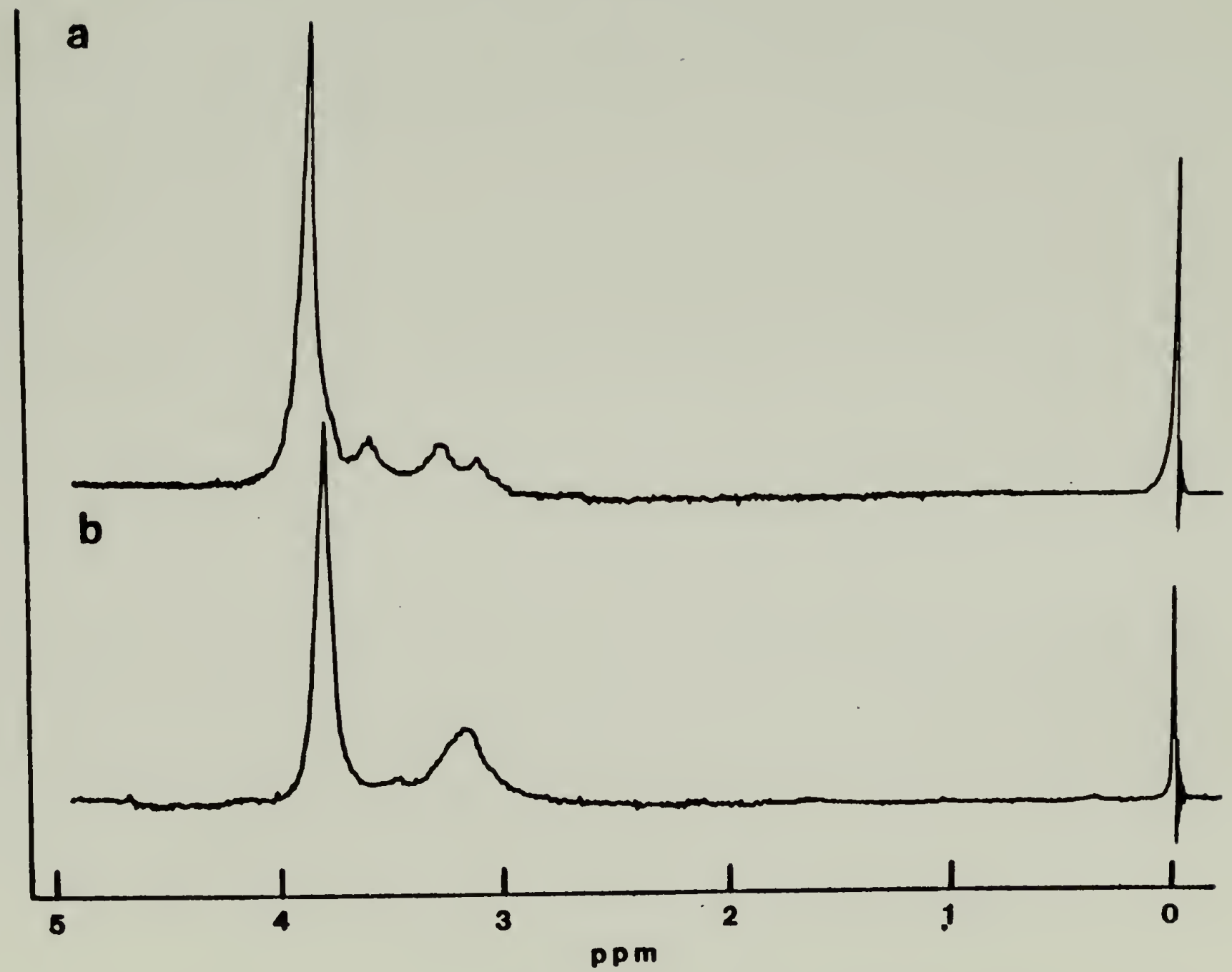


Figure 3-1. Proton NMR Spectra of (a) Isotactic and (b) Syndiotactic Poly(methyl α-bromoacrylate) Recorded at 70°C in 1,1,2,2-Tetrachloroethane

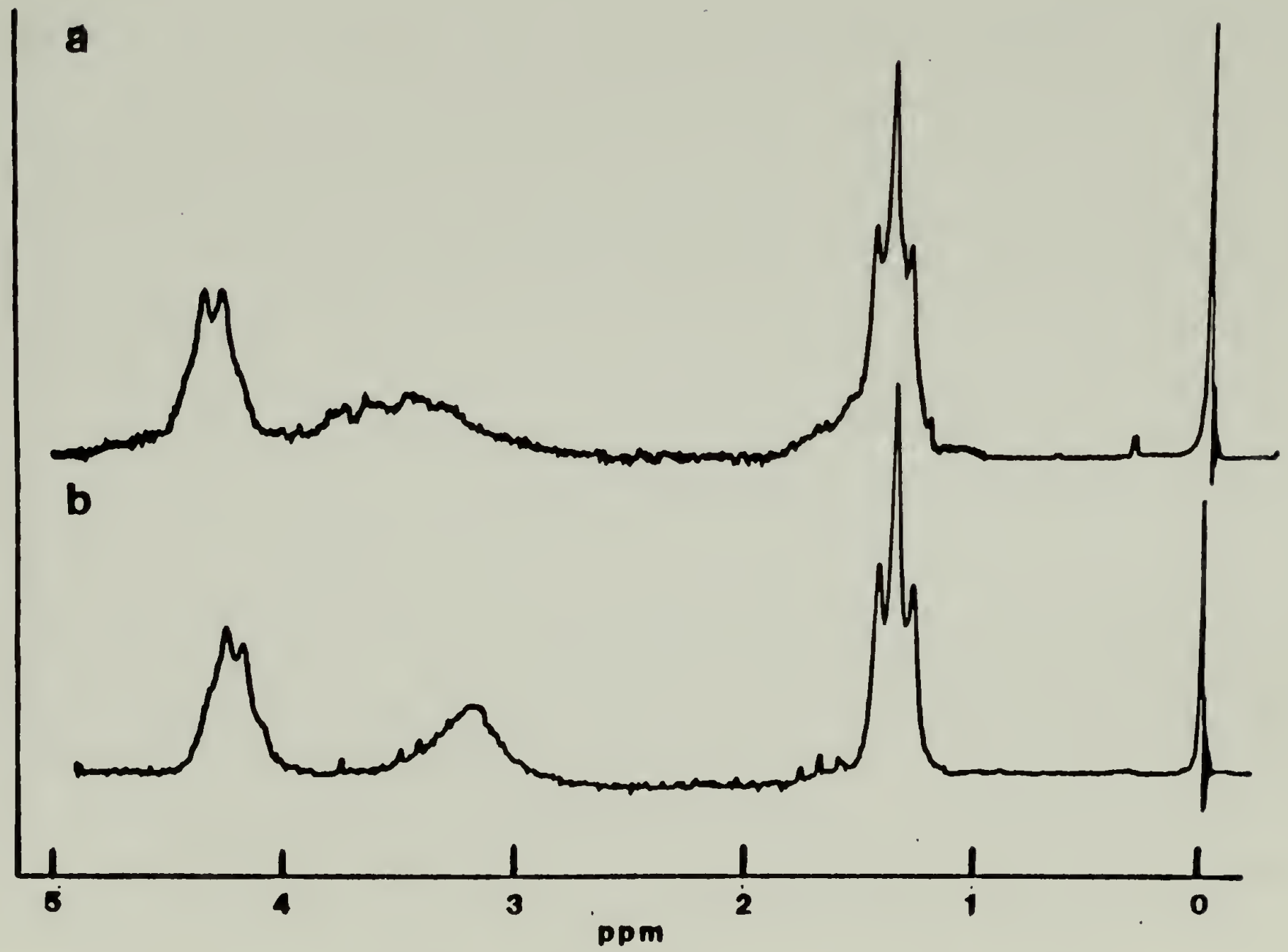


Figure 3-2. Proton NMR Spectra of (a) Isotactic and (b) Syndiotactic Poly(ethyl α-bromoacrylate) Recorded at 70°C in 1,1,2,2-Tetrachloroethane

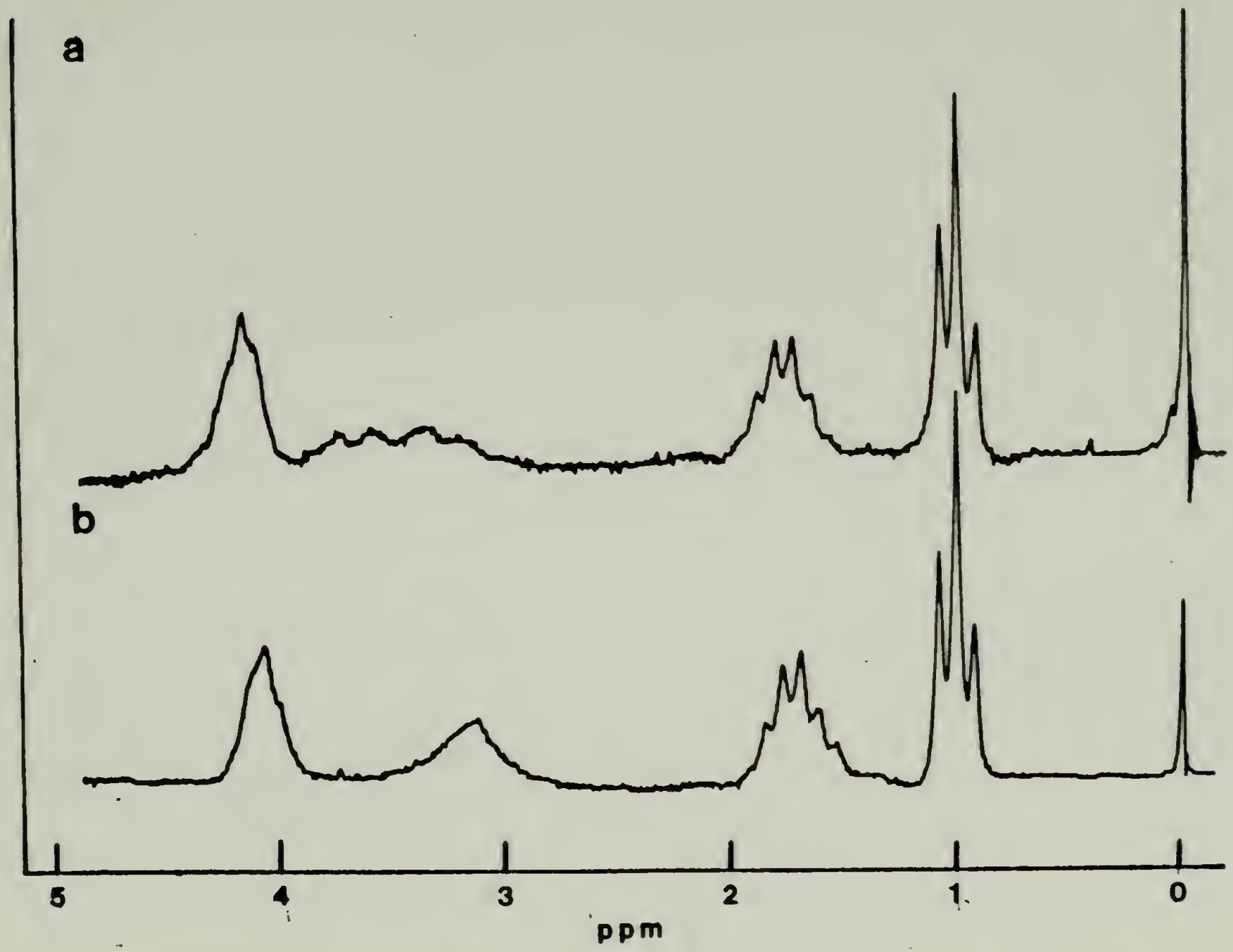


Figure 3-3. Proton NMR Spectra of (a) Isotactic and (b) Syndiotactic Poly(n-propyl α-bromoacrylate) Recorded at 70°C in 1,1,2,2-Tetrachloroethane.

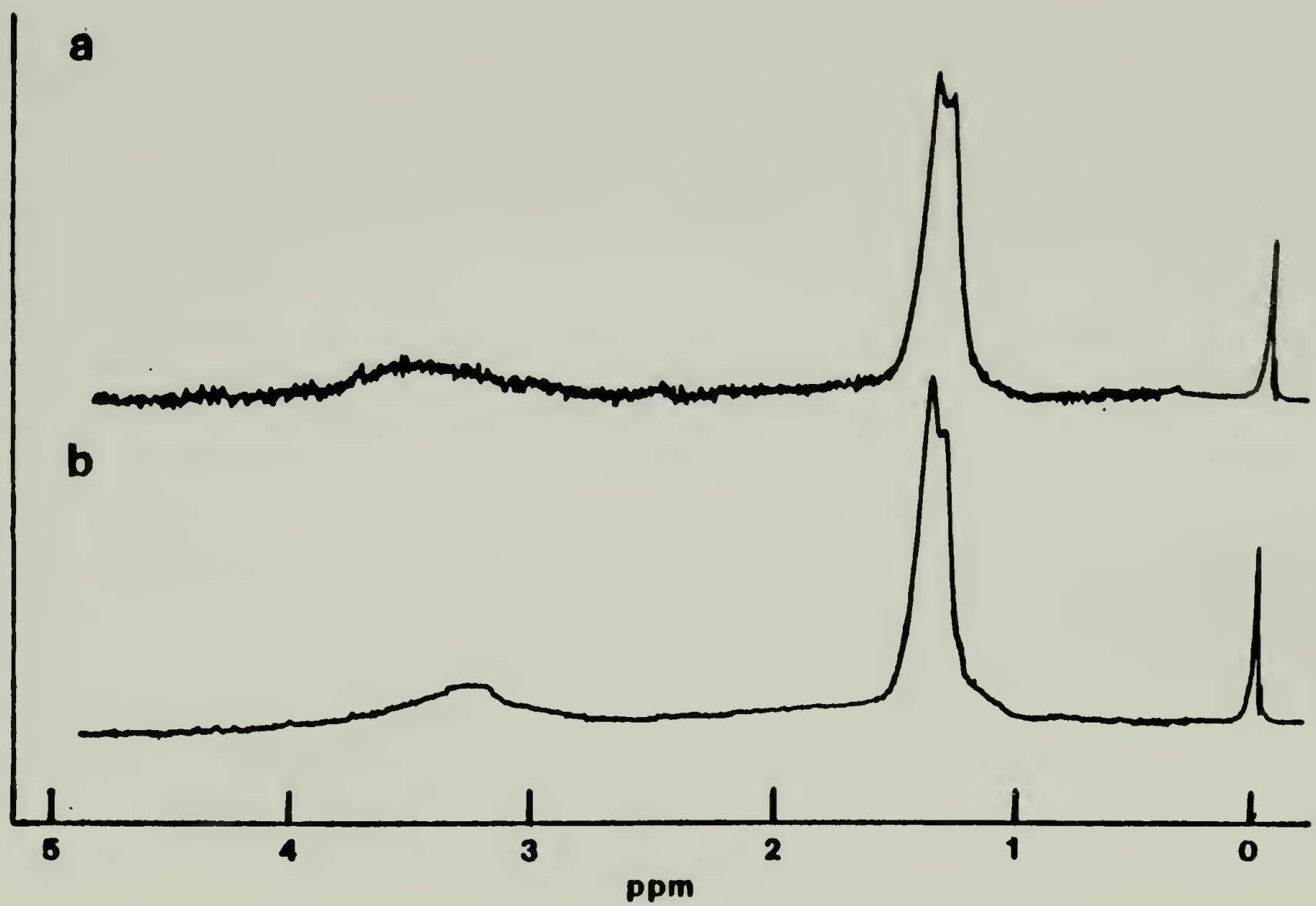


Figure 3-4. Proton NMR Spectra of (a) Isotactic and (b) Syndiotactic Poly(i-propyl α-bromoacrylate) Recorded at 70°C in 1,1,2,2-Tetrachloroethane

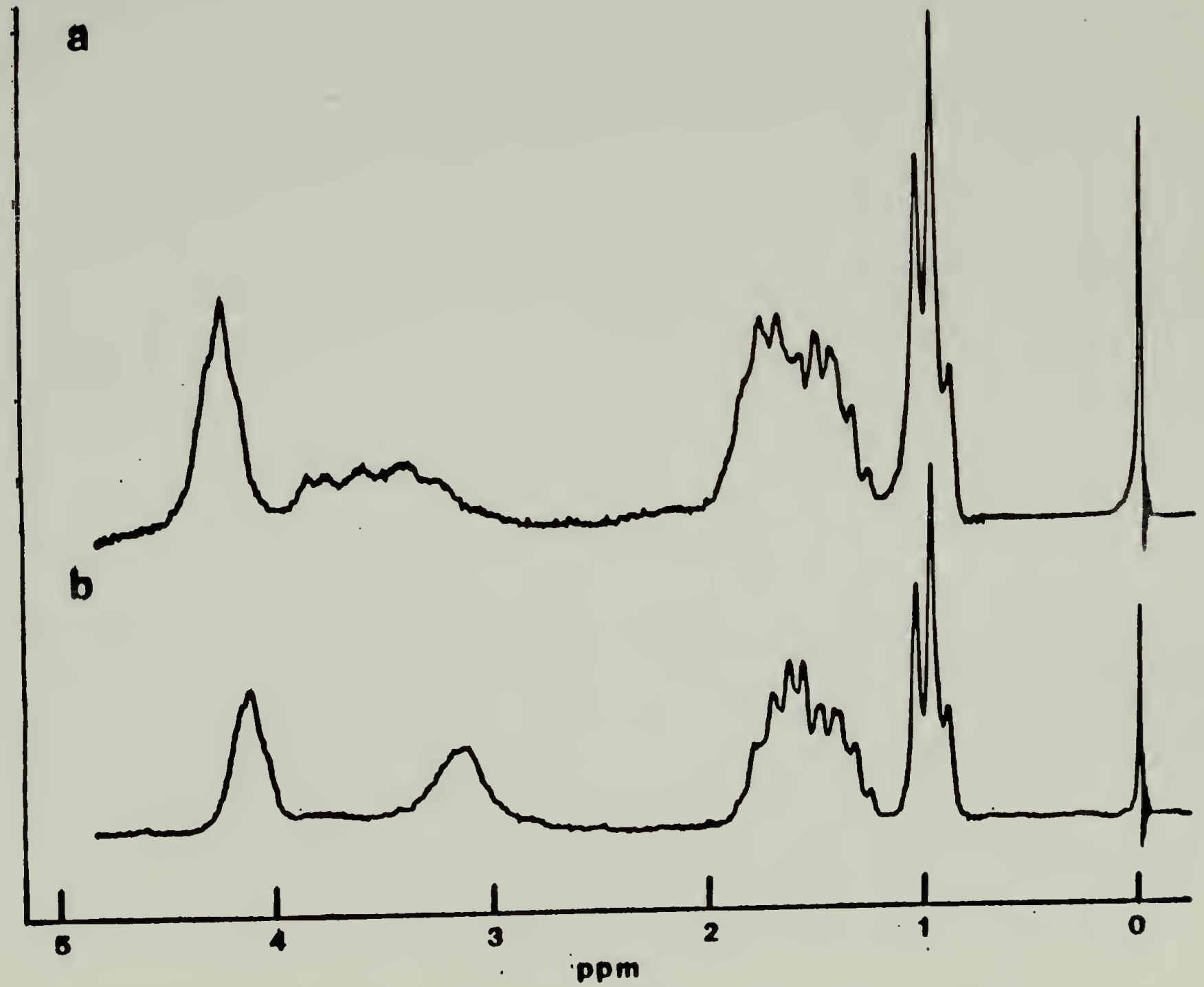


Figure 3-5. Proton NMR Spectra of (a) Isotactic and (b) Syndiotactic Poly(n-butyl α-bromoacrylate) Recorded at 70°C in 1,1,2,2-Tetrachloroethane

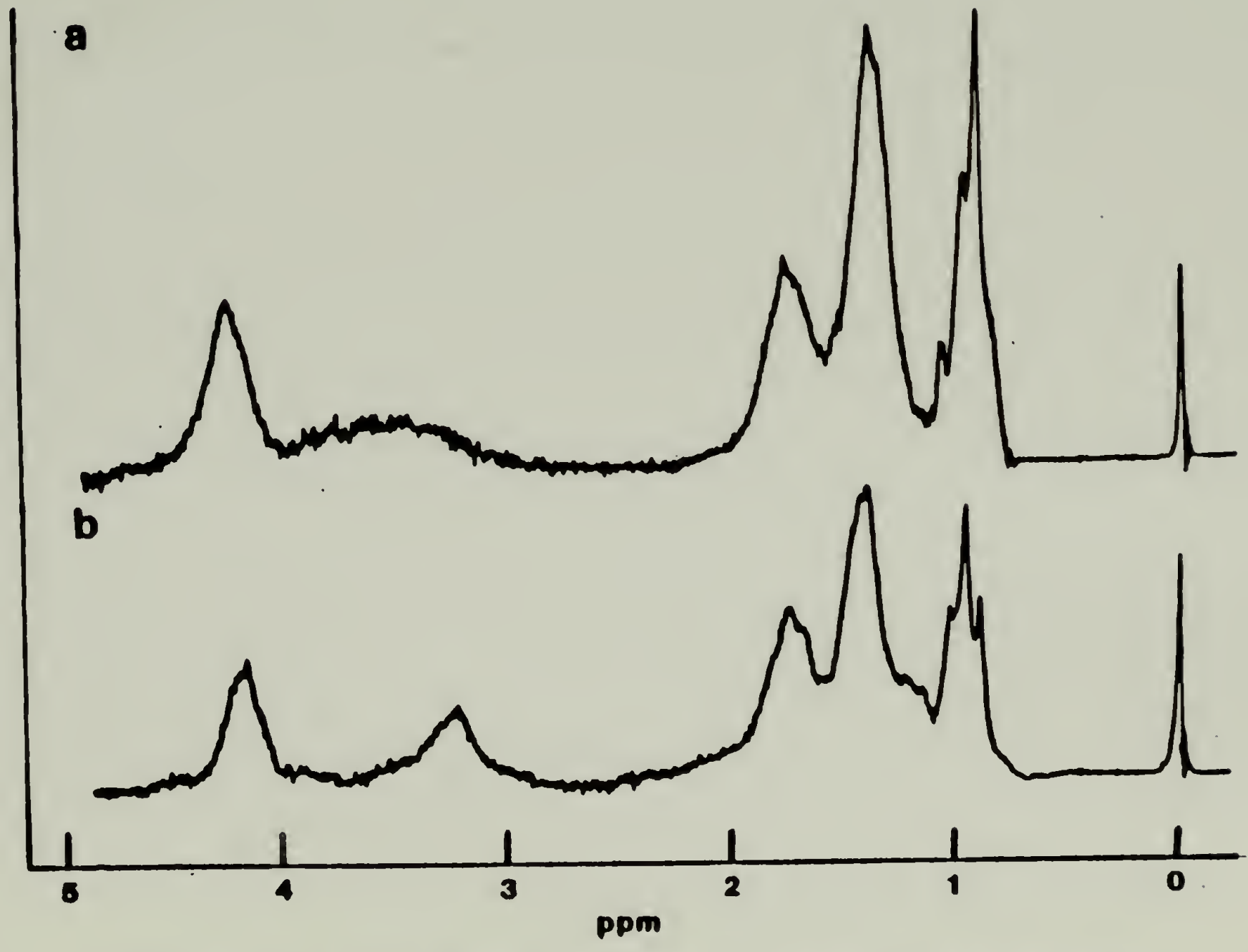


Figure 3-6. Proton NMR Spectra of (a) Isotactic and (b) Syndiotactic Poly(n-pentyl α-bromoacrylate) Recorded at 70°C in 1,1,2,2-Tetrachloroethane

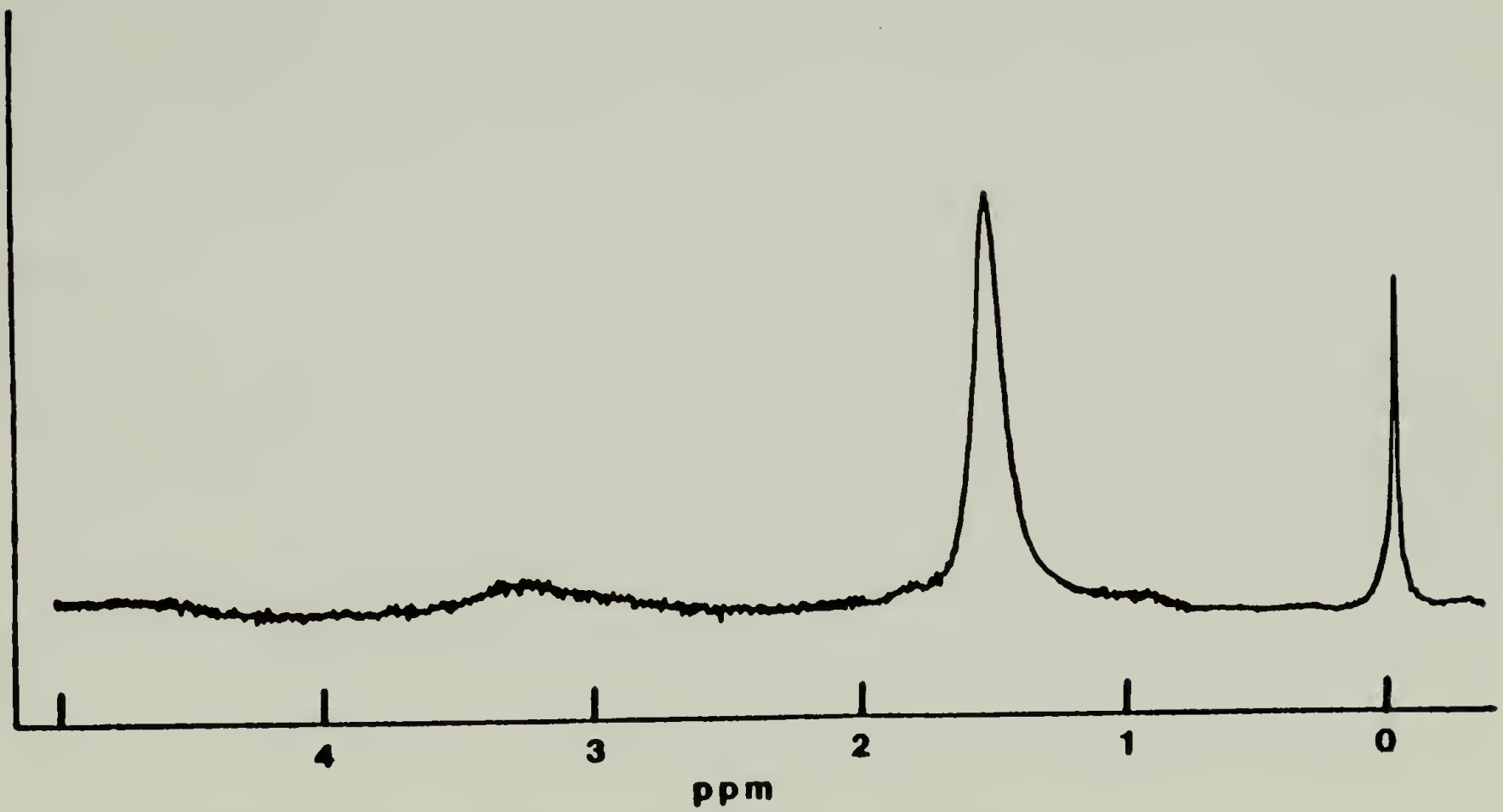


Figure 3-7. Proton NMR Spectrum of Atactic Poly(t-butyl α-bromoacrylate Recorded at 60°C in 1,1,2,2-Tetrachloroethane

co-workers[5] observed a similar relationship between the backbone protons and tacticity for the poly(alkyl α-chloroacrylate)s.

The methoxyl resonance for poly(methyl α-bromoacrylate) appeared as a weak triplet centered at 3.8 ppm downfield from TMS, Figure 3-1. The downfield portion was assigned to isotactic triads, the upfield portion to the syndiotactic triads and the intermediate contribution to the heterotactic triads. These assignments were in agreement with the methoxyl resonance of poly(methyl α-chloroacrylate)[5,8,9] and the α-methyl resonance of poly(methyl methacrylate)[23,24]. Unfortunately, quantitative comparison of the three methoxyl peaks were not possible for the isotactic polymers because of peak overlap with the backbone protons. Quantitative analysis from the ester resonance of the higher esters was not possible due to insufficient peak resolution at 90 mHz. For instance, the methyl resonance from the ester group of poly(ethyl α-bromoacrylate) should have consisted of three triplets corresponding to the isotactic, heterotactic and syndiotactic contributions but observation of Figure 3-2 revealed the presence of only one triplet. Without this peak separation, the determination of tacticity from the ester group resonance was impossible.

The remaining esters displayed a similar lack of peak separation in addition to a considerable amount of further peak overlap originating from the methylene groups of the esters. In Figures 3-3, 3-5 and 3-6 for the n-propyl, n-butyl and n-pentyl esters, respectively, the resonance in the 1 to 2 ppm region arose from middle methylene groups of the ester while the peaks at 3.9 to 4.1 ppm resulted from the first methylene group of each ester. Presumably, if these measurements were

conducted on a higher field strength NMR spectrometer, such as 300 mHz, sufficient peak resolution would have been achieved to measure the tacticity. Dever and co-workers[25] successfully employed 300 mHz NMR spectroscopy for the determination of triad and tetrad tacticity in the methyl, ethyl and i-propyl α-bromoacrylates.

Studies of pentad tacticity by ^{13}C NMR on poly(methyl methacrylate)[26,27] have been very promising while the corresponding studies with 300 ^{1}H NMR have yielded little[28]. As a result, ^{13}C nuclear magnetic resonance spectroscopy was utilized for the measurement of tacticity in the hope of evaluating the pentad as well as tetrad and triad tacticities.

Infrared Spectroscopy

A quantitative correlation between tacticity and infrared spectroscopy was demonstrated for the poly(alkyl α-chloroacrylate)s by Wesslen and Lenz[10] and later by Dever and co-workers[5]. Poly(methyl α-chloroacrylate) was found to have a weak correlation with tacticity only in the carbonyl stretching region at 1742 cm^{-1}. In this investigation, the effects of tacticity were not observed in the infrared spectra of isotactic and syndiotactic poly(methyl α-bromoacrylate). Only a slight broadening in the carbonyl stretching region, 1725 to 1760 cm^{-1}, was seen for the syndiotactic polymers as compared to the isotactic polymers as exhibited in Figures 3-8 through 3-13.

Poly(ethyl α-bromoacrylate), Figure 3-9, was found to have a weak correlation with tacticity in the C-H region at 1440 and 1422 cm^{-1} while poly(i-propyl α-bromoacrylate), Figure 3-11, had a similar

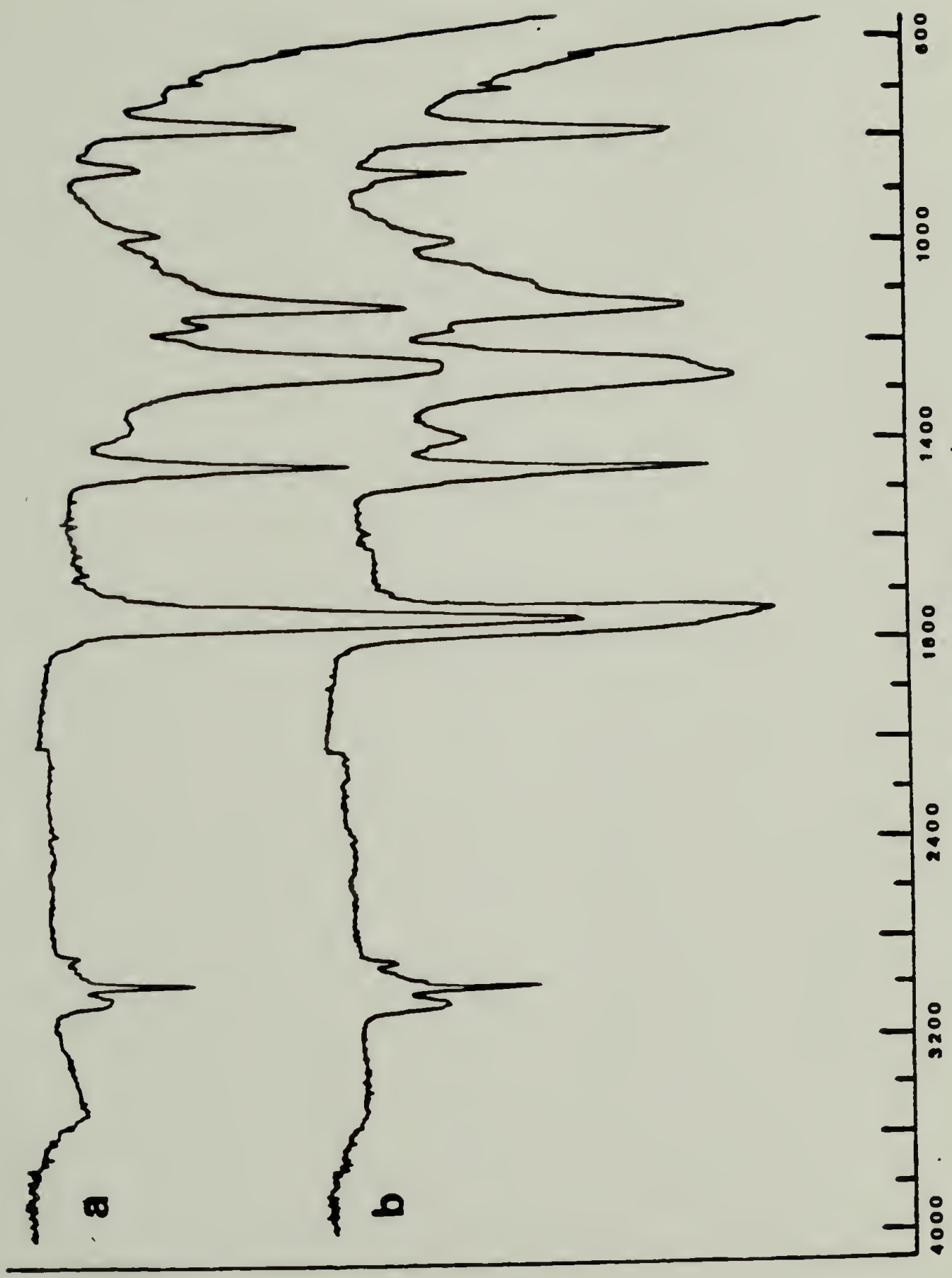


Figure 3-8. Infrared Spectra of (a) Isotactic and (b) Syndiotactic Poly(methyl α-bromoacrylate)

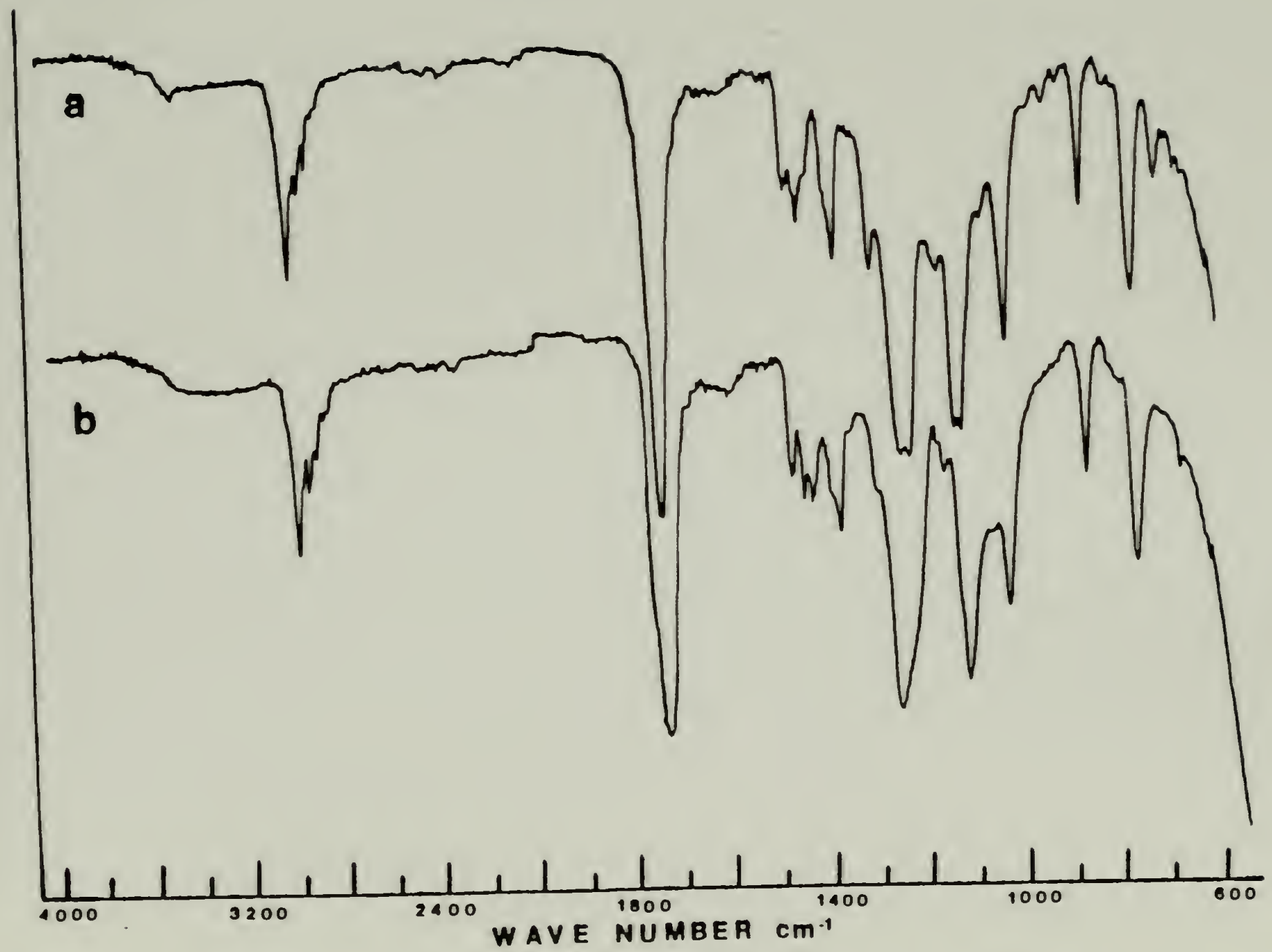


Figure 3-9. Infrared Spectra of (a) Isotactic and (b) Syndiotactic Poly(ethyl α-bromoacrylate)

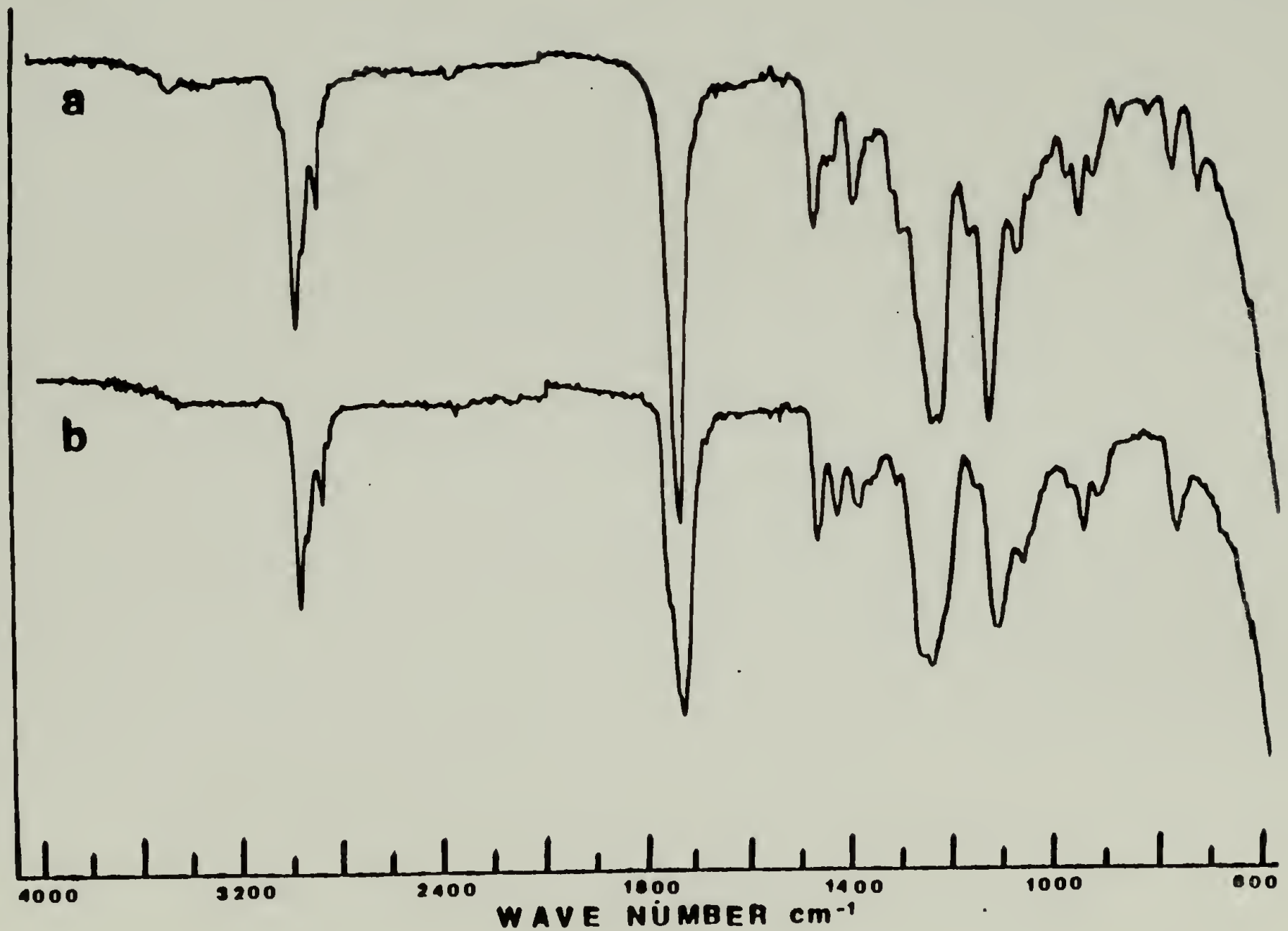


Figure 3-10. Infrared Spectra of (a) Isotactic and (b) Syndiotactic Poly(n-propyl α-bromoacrylate)

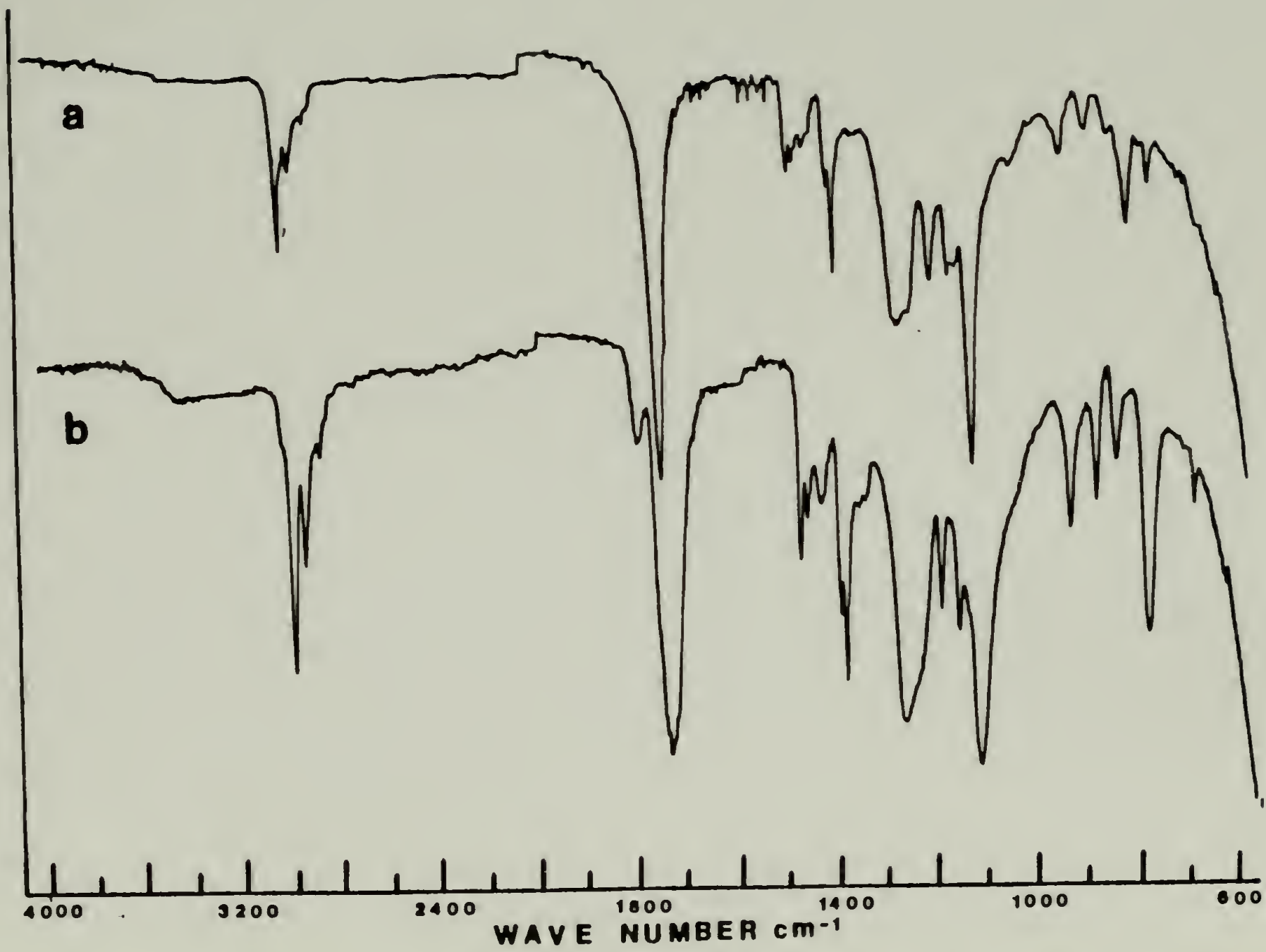


Figure 3-11. Infrared Spectra of (a) Isotactic and (b) Syndiotactic Poly(i-propyl α-bromoacrylate)

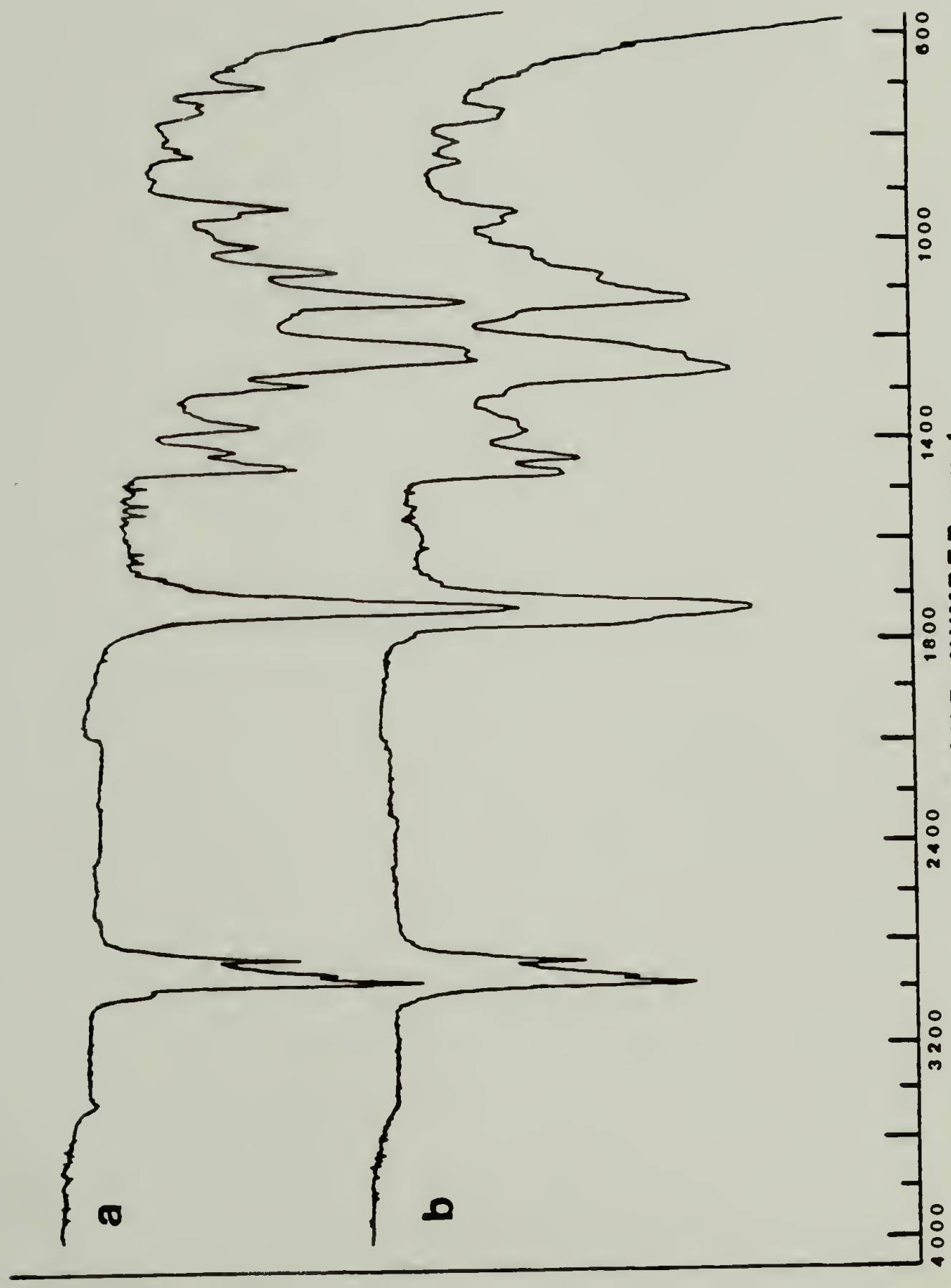


Figure 3-12. Infrared Spectra of (a) Isotactic and (b) Syndiotactic Poly(n-butyl α-bromoacrylate)

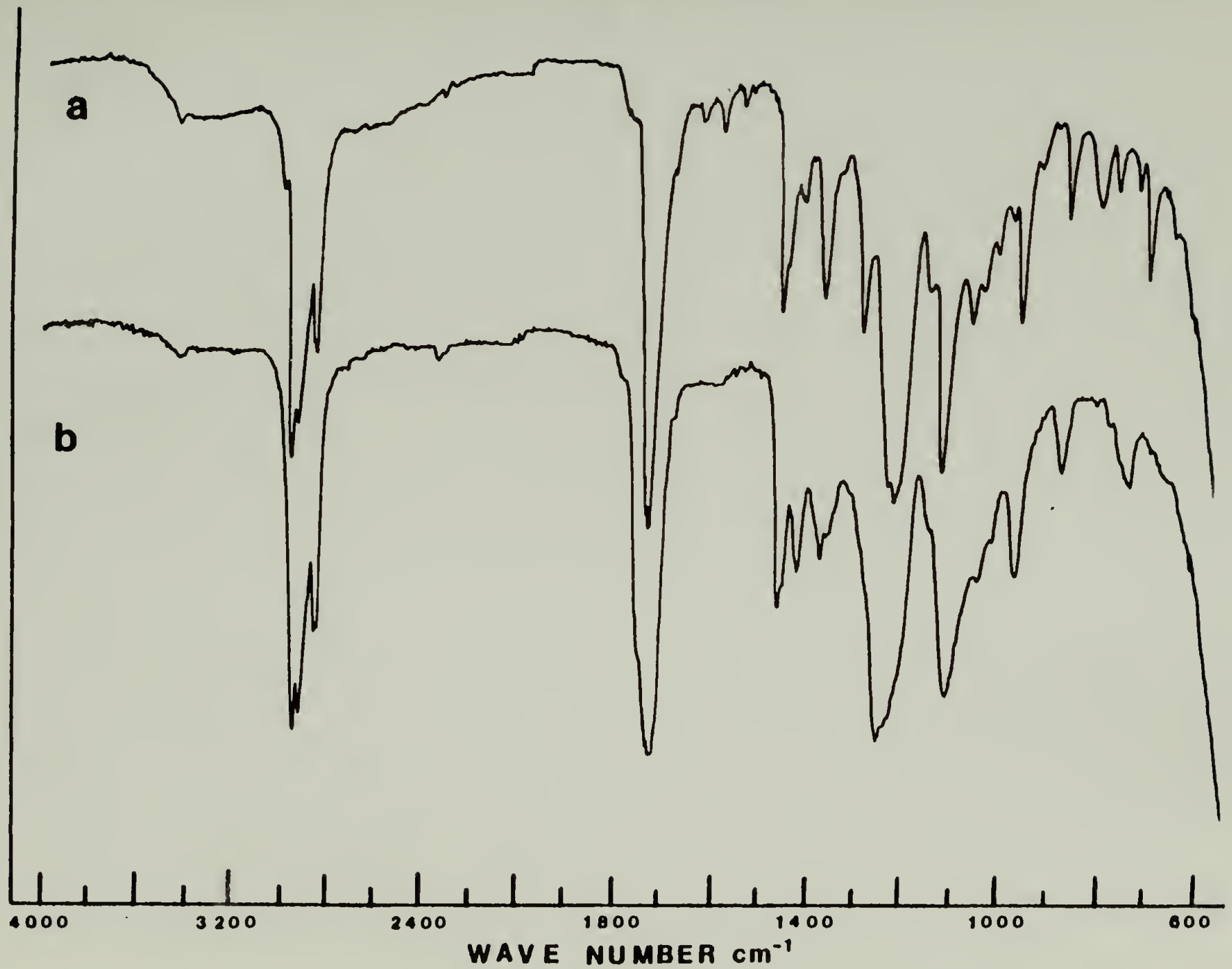


Figure 3-13. Infrared Spectra of (a) Isotactic and (b) Syndiotactic Poly(n-pentyl α-bromoacrylate)

correlation at 1458 and 1424 cm^{-1}. The intensities of these bands were found to vary depending on the stereoregularity of the samples. In particular, the band at the higher wave number increased with increasing isotactic content while the other band decreased. Similar correlations for the n-propyl, n-butyl and n-pentyl esters were found and are listed in Table 3-16. A plot of the absorbance ratios for the isotactic and syndiotactic dependent peaks versus the isotactic dyad content (calculated from the triad values) is given in Figure 3-14. It is apparent that the tacticity of a particular polymer could be determined from a combination of infrared absorption measurements and the plots in Figure 3-14. One major problem with this technique results from the low slopes of the plots which introduce a considerable amount of error. Only slight changes in the absorbance ratio will cause a significant change in the tacticity when estimated from the curves.

Summary and Conclusions

Isotactic, atactic and syndiotactic polymers of the methyl, ethyl, n-propyl, i-propyl, n-butyl and n-pentyl esters of alkyl α-bromoacrylate have been synthesized. These polymers were characterized as to molecular weight, molecular weight distribution and triad tacticity (from Chapter IV). In addition, their 90 mHz proton NMR and infrared spectra were qualitatively interpreted.

A quantitative determination of tacticity was not possible with 90 mHz proton NMR due to severe peak overlap in the ester region but the backbone proton resonance was found to vary qualitatively with tacticity. Also, infrared spectroscopy displayed a semi-quantitative

Table 3-16. Infrared Absorbance Ratios for Six Isotactic, Atactic and Syndiotactic Poly(Alkyl α-bromoacrylate)s

Ester	A_1/A_2	Isotactic	Atactic	Syndiotactic
Ethyl	1440/1422	1.54	1.12	1.00
n-Propyl	1462/1422	1.88	1.40	1.32
i-Propyl	1458/1425	2.02	1.51	1.39
n-Butyl	1462/1431	1.89	1.31	1.15
n-Pentyl	1456/1427	2.21	1.65	1.56

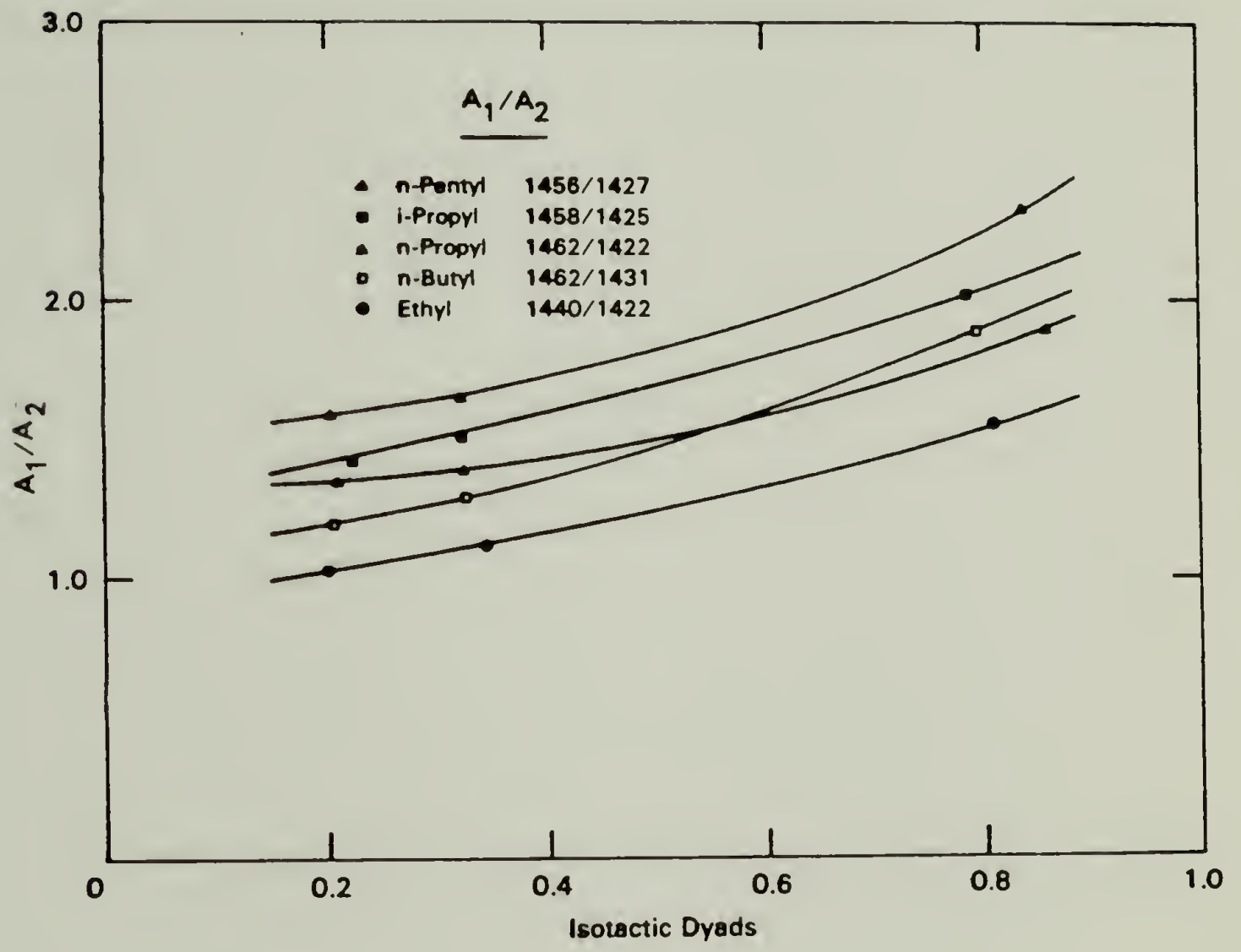


Figure 3-14. Infrared Absorbance Ratios Versus Dyad Tacticity for Poly(alkyl α-bromoacrylate)s

correlation with tacticity in the C-H bending region. The evaluations of the glass transition temperatures were not possible for any of the polymers due to their low thermal stability. This aspect will be discussed in greater detail in Chapter V of the dissertation.

The isotactic polymers were prepared by a modified Grignard complex consisting of the reaction product between methyl magnesium chloride and benzalacetophenone. The polymerization reactions were heterogeneous and anionic in nature and produced polymers with number average molecular weights between 31,000 and 93,000. The polydispersities were all within the range of 2.99 to 3.35. The isotactic triad contents were calculated from the pentad tacticity of the ^{13}C carbonyl carbon resonance (see Chapter IV) and varied from 60 to 74% depending on the ester.

The atactic polymers were synthesized at 50°C employing decanoyl peroxide as the free radical initiator. The calculated rr values were all between 43 and 46% with the number average molecular weights in the 15,000 to 44,000 range and the polydispersities were between 1.73 and 3.44.

The syndiotactic polymers prepared at -40°C with ultraviolet light and benzoin as a photoinitiator generally had the smallest molecular weight distributions, 1.63 to 2.17, with the number average molecular weights between 29,500 and 63,000. The calculated syndiotactic triad tacticities ranged from 0.60 to 0.66%.

Due to the failure of t-butyl α-bromoacrylate to polymerize with either the modified Grignard reagent or in solution, it was polymerized only at 50°C in the bulk state with decanoyl peroxide.

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C H A P T E R I V

THE STEREOREGULARITY OF POLY(ALKYL α-BROMOACRYLATE)S BY 19 mHz ^{13}C NUCLEAR MAGNETIC RESONANCE

Introduction

The analysis of polymer tacticity until very recently had almost always been determined by proton nuclear magnetic resonance spectroscopy. The advent of vastly improved ^{13}C NMR instrumentation has contributed to the increased importance of this spectroscopy in the last few years. The initial studies of polymer tacticity were conducted by Bovey and co-workers on poly(methyl methacrylate)[1]. The influence of the polymer configuration was observed at four different carbon resonances: the backbone methylene carbon, the α-methyl group carbon, the carbonyl carbon and the quaternary carbon. The α-methyl carbon resonance displayed three peaks which consisted of the same triad pattern as the α-methyl proton spectrum. In other words, the mm triad represented the downfield portion, the rr triad represented the upfield portion and the mr triad corresponded to the intermediate field position. The resonance from the carbonyl carbon spectrum revealed some pentad splitting but could be interpreted in terms of triads only. Insufficient resolution and excessive baseline noise prevented a quantitative determination of tacticity from any of the four carbon resonances.

Although ^{13}C NMR studies on the stereochemistry of other polymers such as: polystyrene[1], polypropylene[1-3], poly(vinyl methyl ether)[1,4], poly(vinyl chloride)[5,6], and polyacrylonitrile[7],have been conducted,

further investigations concerning the tacticity of poly(methyl methacrylate) have not appeared in the literature. There has, however, been a very recent investigation by Hatada, Kitayama and Lenz[8] concerning the stereochemistry of isotactic and syndiotactic poly(alkyl α-chloroacrylate)s with 25 mHz ^{13}C NMR spectroscopy. They were able to assign all six tetrad values from the backbone methylene carbon resonance of the isotactic and syndiotactic samples of poly(methyl α-chloroacrylate) and poly(i-propyl α-chloroacrylate). For all polymers, the assignments were in the order:

$$rrr < rmr < rrm < mmr < mrm < mmm$$

with increasing field strength. The tacticity values from the above assignments compared exceptionally well with those from 100 mHz ^{1}H NMR spectroscopy of the identical samples[9].

Complete pentad assignments were not possible from either the carbonyl carbon or the quaternary carbon resonances for any of the samples investigated. The highest degree of success was achieved with the quaternary carbon resonance where seven of the possible ten peaks were assigned. The fractions of tactic pentads were calculated by using first-order Markovian statistics for the isotactic polymers and Bernoullian statistics for the syndiotactic polymers in conjunction with the propagation statistics obtained by 300 mHz ^{1}H NMR spectroscopy[9]. Thus, with support of these calculated pentad tacticities, the seven observed peaks could be interpreted in terms of pentad tacticities.

For the carbonyl carbon resonance, it was possible only to interpret the peaks in terms of triads although the resolution into pentad tacticity was evident for several of the peaks. The estimated triad tacticities were in good agreement with those calculated from the tetrad tacticities of the backbone methylene carbon resonance as well as with the triad tacticities measured by 300 mHz ^{1}H NMR spectroscopy[9].

It is fairly well documented that the ^{13}C spin-lattice relaxation time is longer for isotactic sequences than for syndiotactic sequences[10-13]. Hatada and co-workers[14] found a longer ^{13}C spin-lattice relaxation time for the mmm tetrad peak in isotactic poly(ethyl α-chloroacrylate) as compared to the rrr peak in the corresponding syndiotactic polymer but no significant differences were seen for the spin-lattice relaxation times within the same polymer. In view of this observation, any differences in the spin-lattice relaxation times were considered to be insignificant in the present investigation.

All of the ^{13}C NMR experiments in this investigation, as well as a majority of all other ^{13}C NMR experiments, utilized a proton decoupling technique to eliminate proton-induced splittings and to greatly simplify the ^{13}C spectrum. The use of proton decoupling gives rise to a nuclear Overhauser effect (NOE). In the case of polymers, the NOE is apparently identical for all aliphatic carbon nuclei in a given polymer and therefore, the integrated intensities of these peaks can be compared directly[15,16]. In any event, if the carbons differ in only the steric configuration of the neighboring units, the peak intensities are directly comparable. Thus, the NOE of a carbonyl carbon in an isotactic unit should be equivalent to that of a carbonyl carbon in a

syndiotactic unit of the same polymer. Consequently, the integrated intensities can be used without the need for any modifications.

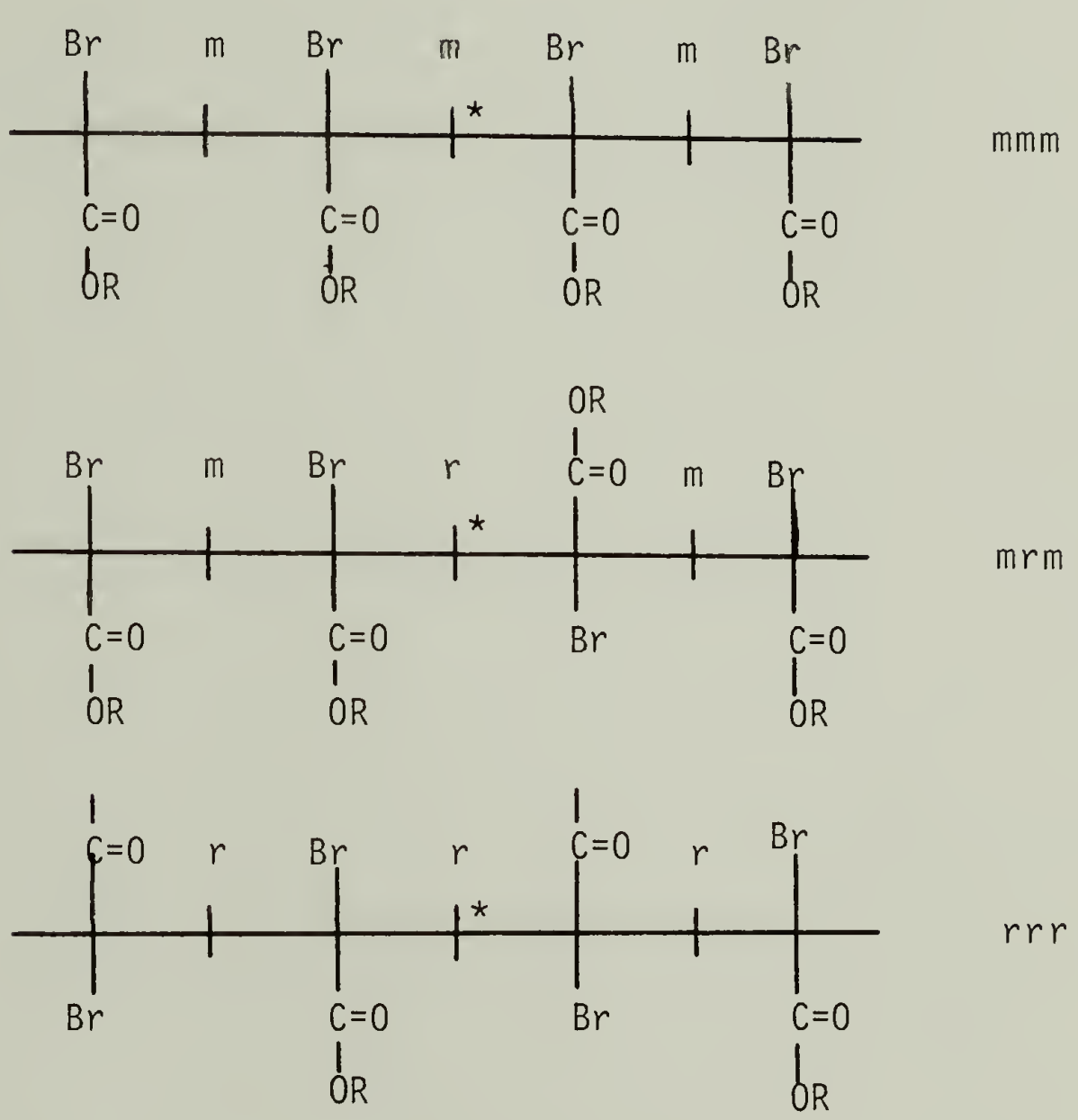
Experimental

Polymer preparation. The polymers examined in this investigation were synthesized by anionic and free-radical initiators as described in Chapters II and III. A modified Grignard complex (anionic) was employed for the preparation of the isotactic polymers while the syndiotactic polymers were synthesized at -40°C using benzoin as a photosensitizer and ultraviolet light as the means of initiation.

^{13}C nuclear magnetic resonance. The ^{13}C 19 mHz NMR spectra were obtained using a Varian CFT-20 Fourier transform spectrometer. When solubility permitted, polymer solutions up to 20-30% (w/v) in deuterated chloroform were used. Due to the limited solubility of poly(i-propyl α-bromoacrylate), sample 31, a 50% solution of 1,1,2,2-tetrachloroethane in deuterated chloroform was employed. All measurements were conducted at 35°C in 8-mm high resolution NMR tubes with tetramethylsiloxane (TMS) as the internal standard. The instrumental parameters utilized for all of the spectra were: an acquisition time of 1.023 seconds, a pulse width of 15 microseconds, a pulse delay of one second and a number of accumulated transients between 20,000 and 40,000. All chemical shifts were expressed in parts per million downfield from TMS.

Resolution of the backbone methylene carbon resonance. The ^{13}C resonance of the backbone methylene carbons in the isotactic, atactic and syndiotactic poly(alkyl α-bromoacrylate)s should be split into six

peaks corresponding to the six possible sequences of configurational tetrads, three of which are represented below:



The remaining three possible tetrad sequences are rmr, mmr, and rrm. Figures 4-1 through 4-5 display the backbone methylene carbon resonance for the ethyl, n-propyl, i-propyl, n-butyl and n-pentyl esters, respectively.

The strongest peaks in the spectra of the predominately isotactic and syndiotactic polymers were assigned directly to the mmm and rrr

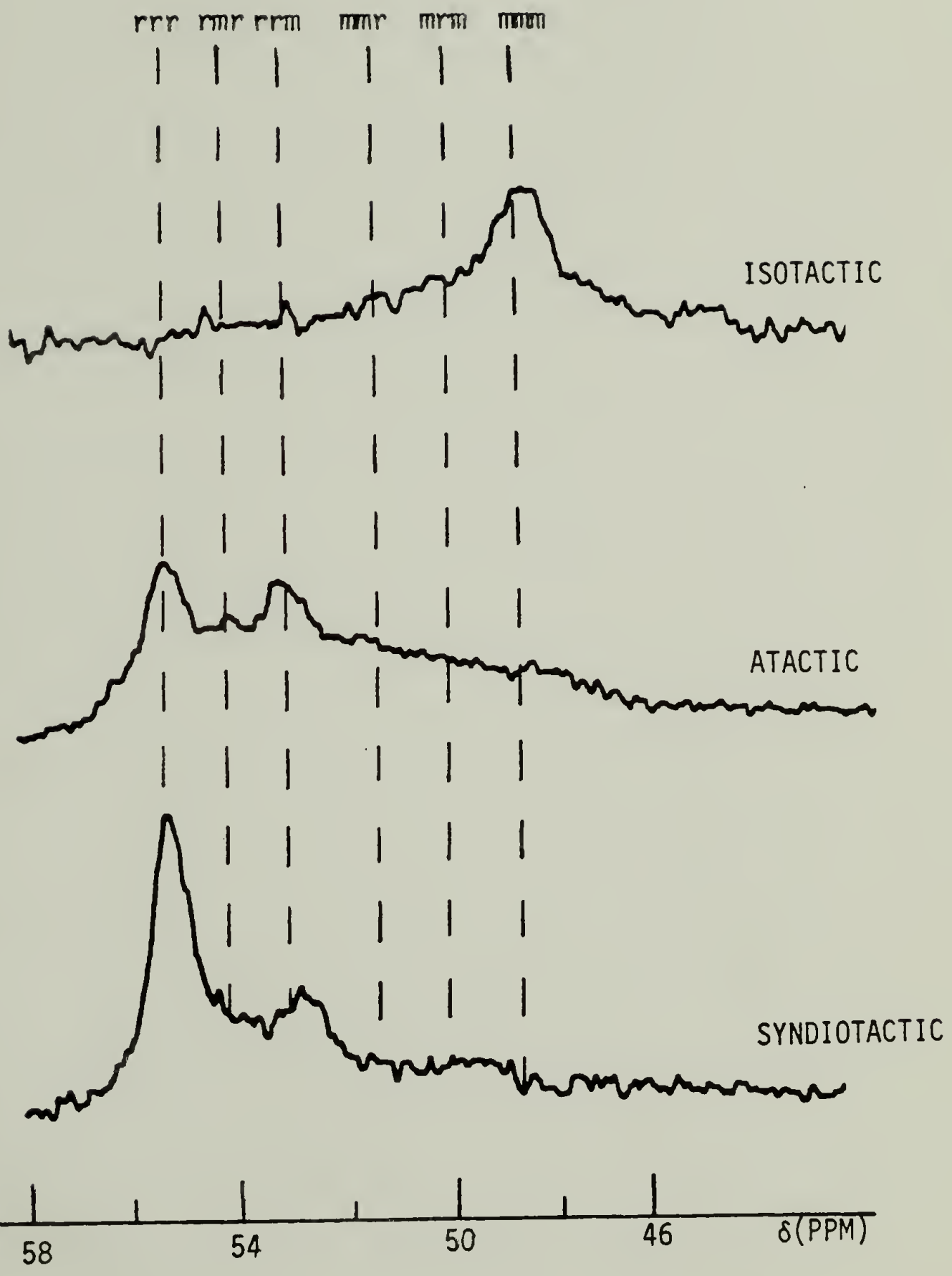


Figure 4-1. The Backbone Methylene Carbon Resonance of Poly(ethyl α-bromoacrylate) in ppm Relative to TMS

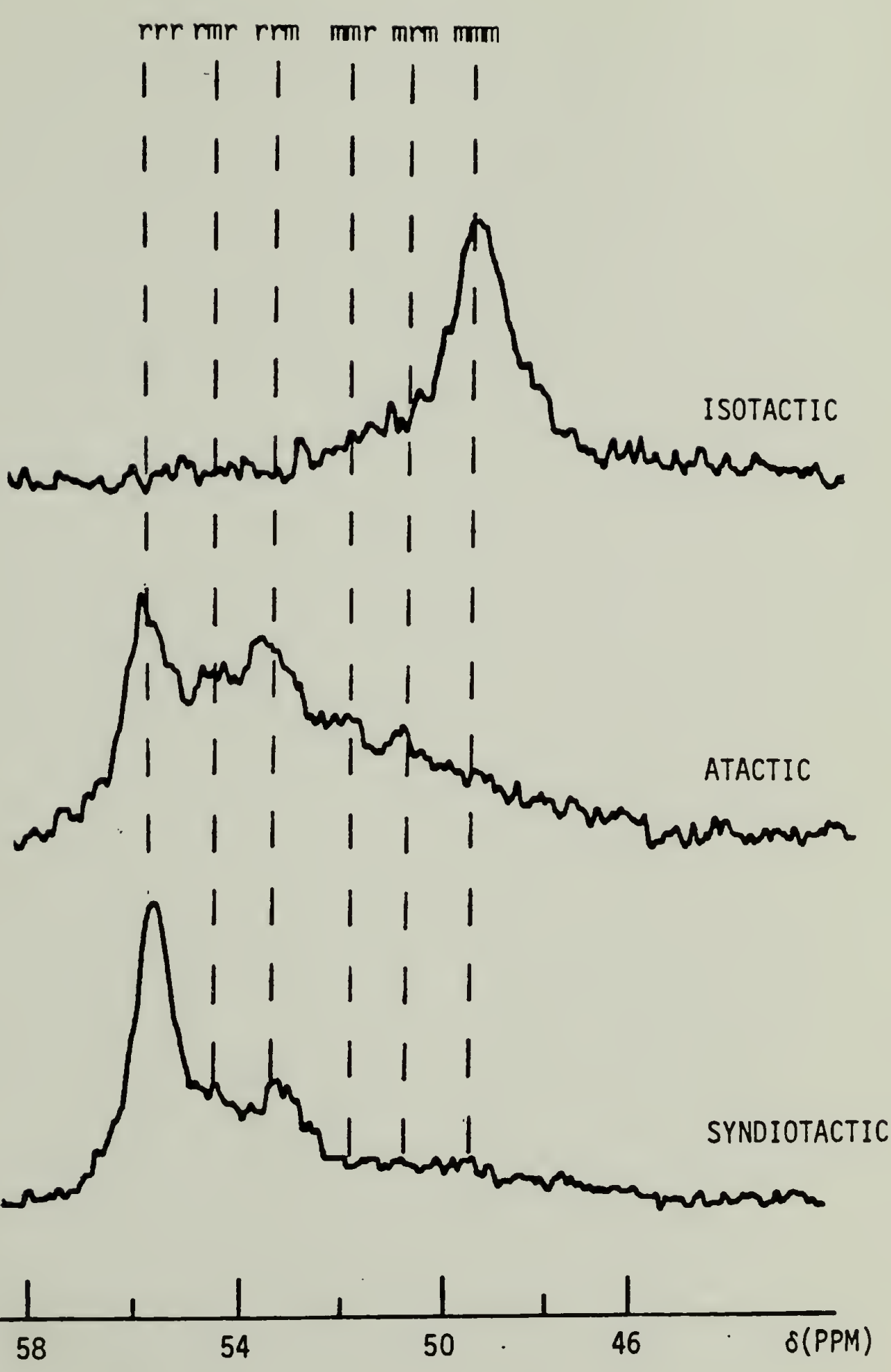


Figure 4-2. The Backbone Methylene Carbon Resonance of Poly(n-propyl α-bromoacrylate) in ppm Relative to TMS

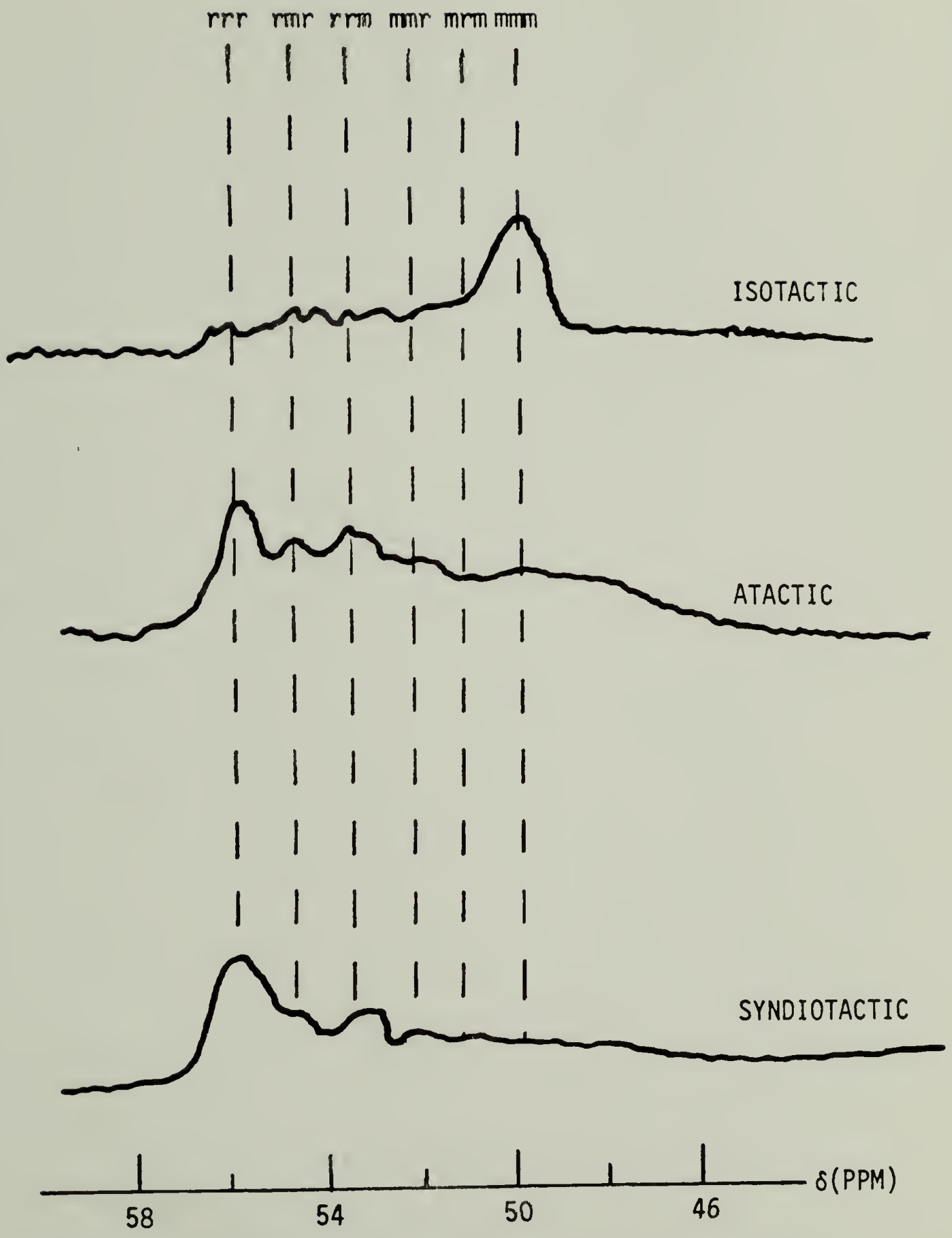


Figure 4-3. The Backbone Methylene Carbon Resonance of Poly(i-propyl α-bromoacrylate) in ppm Relative to TMS

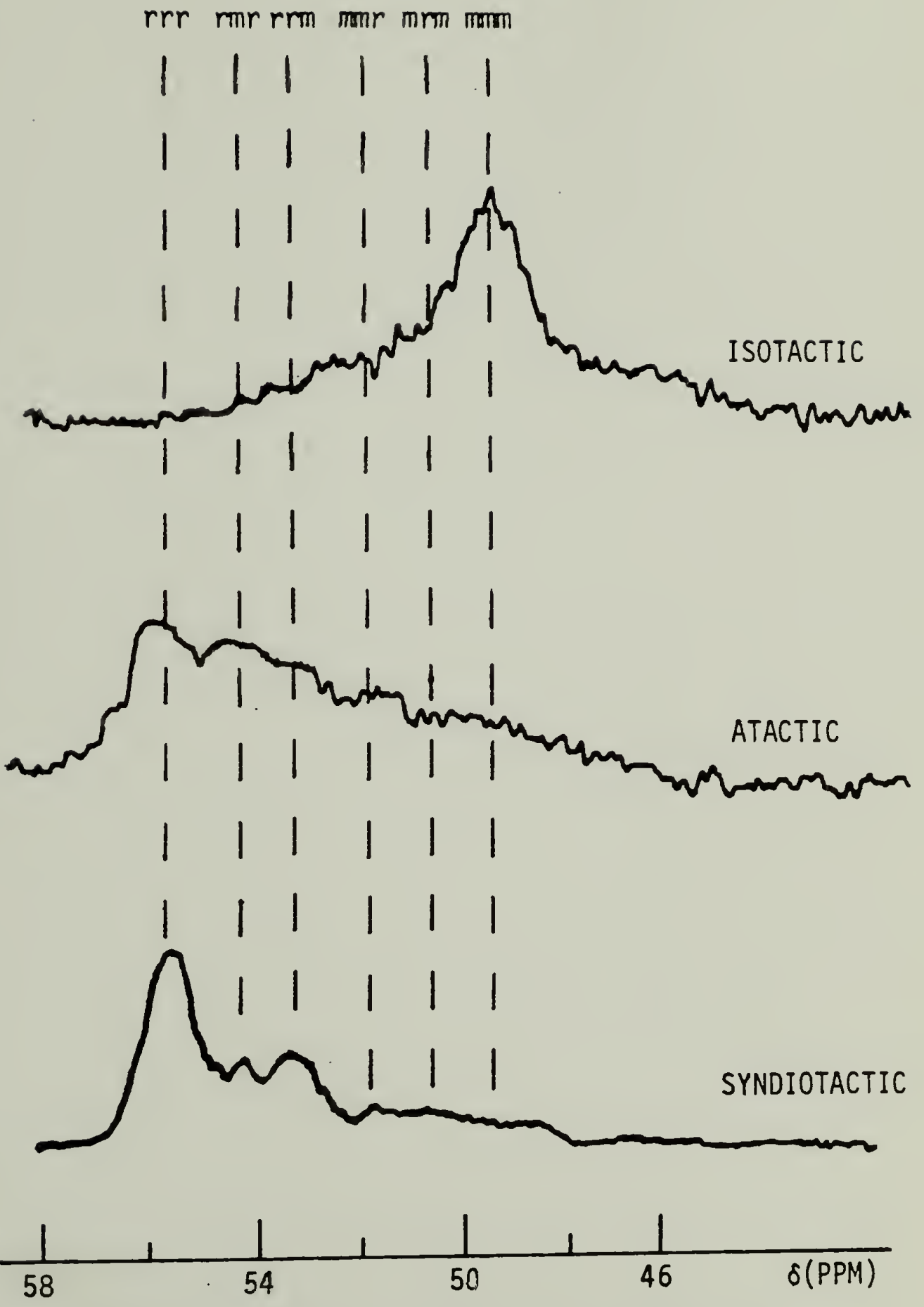


Figure 4-4. The Backbone Methylene Carbon Resonance of Poly(n-butyl α-bromoacrylate) in ppm Relative to TMS

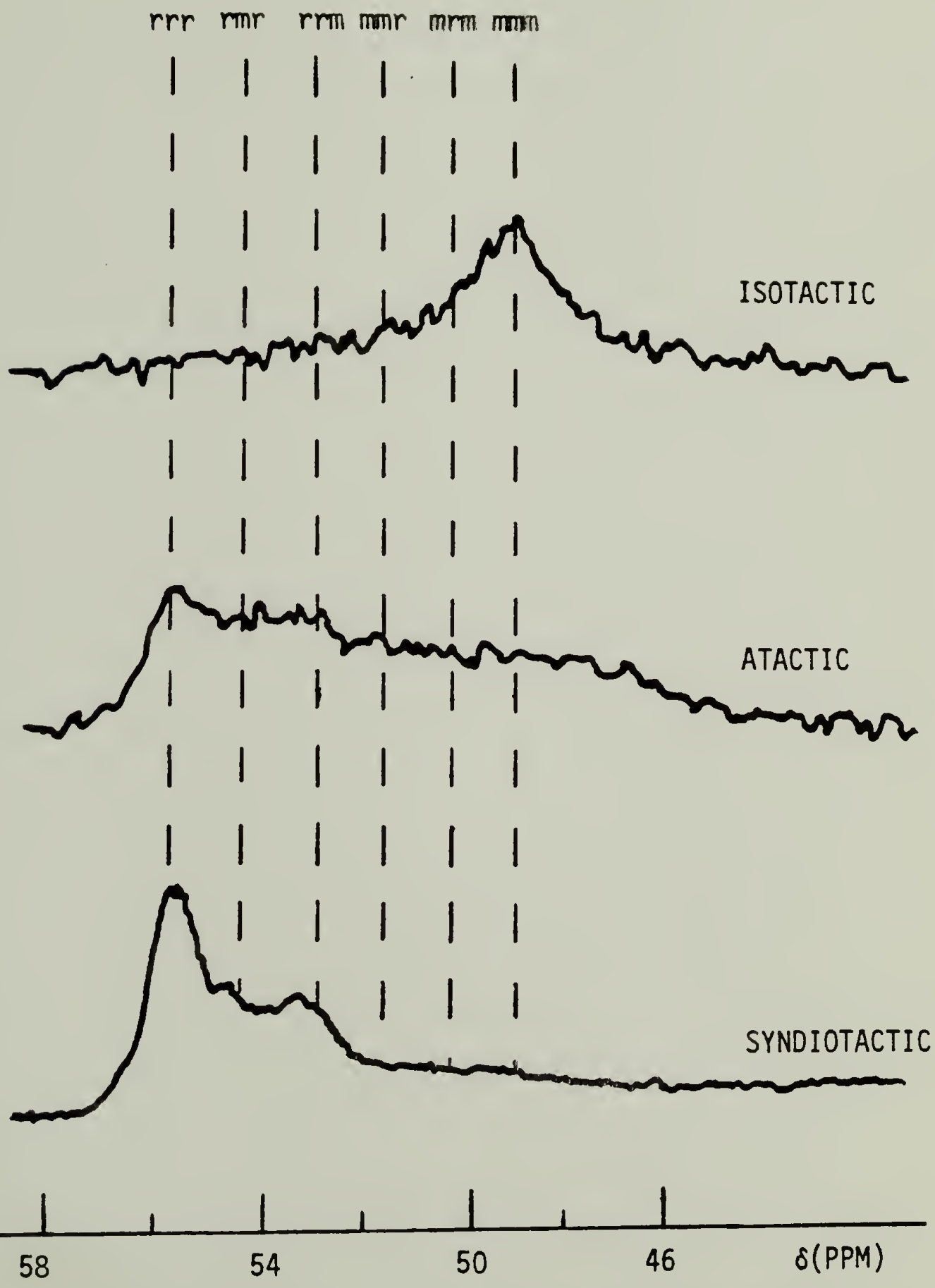


Figure 4-5. The Backbone Methylene Carbon Resonance of Poly(n-pentyl α-bromoacrylate) in ppm Relative to TMS

tetrads. The assignments of the remaining four sequences were accomplished by assuming that the next strongest peak in the syndiotactic polymer represented the rrm sequence and the next strongest peak for the isotactic polymer corresponded to the mmr sequence. Finally, based on deshielding considerations, the rmr and mrm peaks were assigned closest to the rrr and mmm resonances, respectively.

Based on elementary statistical principles the occurrence of all sequences, tetrad or otherwise, are controlled by certain necessary relationships which are completely independent of the configurational statistics produced by any one mechanism. There are two necessary relationships for tetrads and they are given by equations 1 and 2[17].

$$mmm + mmr + mrm + rmr + rrm + rrr = 1 \qquad (1)$$

$$mmr + 2(rmr) = mrr + 2(mrm) \qquad (2)$$

The second equality functions as an excellent test for the peak assignments since it is independent of any propagation model such as Bernoullian or Markovian. Thus, any set of peak assignments which do not satisfy equation (2) must be incorrect. This requirement has been met reasonably well for the peak areas of the six tetrads for all of the polymers investigated (Figures 4-1 through 4-5) where the agreement was generally within 5%. A deviation of 5% or less was certainly acceptable when one considers the error involved in the experimental technique. The major portion of the experimental error originated from the excess baseline noise in ^{13}C NMR spectra which can be alleviated only by increasing either (or both) the sample concentration or the number of spectral scans during the NMR measurements.

With a considerable degree of confidence, the peaks were assigned in the following order as a function of increasing field strength:

$$rrr < rmr < rrm < mmr < mrm < mmm$$

These assignments were in exact agreement with those from a similar analysis on a series of poly(alkyl α-chloroacrylate) esters by Hatada, Kitayama and Lenz[8]. Table 4-1 lists the tetrad chemical shifts for all esters except the methyl where peak assignments were not possible due to peak overlap of the methyl ester carbon and backbone methylene carbon resonance. In a similar manner, 90 mHz NMR spectroscopy revealed that the backbone methylene and methyl group proton resonance of isotactic poly(methyl α-bromoacrylate) overlapped each other as shown in Figure 3-1 of Chapter III.

The measured tetrad intensities (relative peak areas) are collected in Tables 4-2 through 4-6 for the ethyl, n-propyl, i-propyl, n-butyl and n-pentyl esters, respectively. In addition, these tables contain the corresponding triad intensities calculated from the experimentally determined tetrads using the following equations:

$$mr = mmr + 2(rmr) \equiv mrr + 2(mrm) \qquad (2)$$

$$rr = rrr + 1/2(rrm) \qquad (3)$$

$$mm = mmm + 1/2(mmr) \qquad (4)$$

It should be pointed out that the equation used to calculate the mr triad, equation (2), is one of the necessary tetrad relationships.

Resolution of the carbonyl carbon resonance. The carbonyl carbon resonance of isotactic, atactic and syndiotactic poly(methyl α-bromoacrylate) is displayed in Figure 4-6. The influence of the polymer configuration on the relative peak intensities associated with each

Table 4-1. Tetrad Chemical Shifts for Backbone Methylene Carbon Resonance of Five Poly(alkyl α-bromoacrylate) Esters[a]

Ester	rrr	rmr	rrm	mmr	mrm	mmm
Ethyl	55.19	54.02	52.46	50.72	49.96	48.51
n-Propyl	55.80	54.20	53.10	50.87	49.51	48.90
i-Propyl	54.93	53.01	51.72	49.62	47.90	46.17
n-Butyl	55.53	53.80	52.61	51.48	50.01	48.49
n-Pentyl	55.60	54.02	52.86	51.62	50.11	48.44

a. in ppm relative to TMS

Table 4-2. Relative Tetrad and Calculated Triad Intensities from the Backbone Methylene Carbon Resonance of Poly(ethyl α-bromoacrylate).

Tacticity	Tetrads						Triads[a]		
	rrr	rmr	rrm	mmr	mrm	mmm	rr	mr	mm
Isotactic	0.04	0.04	0.06	0.17	0.09	0.60	0.08	0.24	0.68
Atactic	0.30	0.16	0.28	0.14	0.08	0.04	0.44	0.45	0.11
Syndiotactic	0.52	0.14	0.23	0.05	0.04	0.02	0.64	0.32	0.04

a. calculated from tetrads

Table 4-3. Relative Tetrad and Calculated Triad Intensities from the Backbone Methylene Carbon Resonance of Poly(n-propyl α-bromoacrylate).

Tacticity	Tetrads						Triads[a]		
	rrr	rmr	rrm	mmr	mrm	mmm	rr	mr	mm
Isotactic	0.02	0.02	0.05	0.15	0.06	0.70	0.04	0.19	0.77
Atactic	0.29	0.17	0.27	0.13	0.09	0.05	0.43	0.45	0.12
Syndiotactic	0.49	0.16	0.24	0.05	0.04	0.02	0.61	0.35	0.04

a. calculated from tetrads

Table 4-4. Relative Tetrad and Calculated Triad Intensities from the Backbone Methylene Carbon Resonance of Poly(i-propyl α-bromoacrylate).

Tacticity	Tetrads						Triads[a]		
	rrr	rmr	rrm	mmr	mrm	mmm	rr	mr	mm
Isotactic	0.03	0.03	0.10	0.20	0.10	0.54	0.08	0.28	0.64
Atactic	0.30	0.17	0.29	0.13	0.07	0.04	0.43	0.46	0.11
Syndiotactic	0.45	0.14	0.25	0.08	0.06	0.02	0.58	0.36	0.06

a. calculated from tetrads

Table 4-5. Relative Tetrad and Calculated Triad Intensities from the Backbone Methylene Carbon Resonance of Poly(n-butyl α-bromoacrylate).

Tacticity	Tetrads						Triads[a]		
	rrr	rmr	rrm	mmr	mrm	mmm	rr	mr	mm
Isotactic	0.02	0.03	0.08	0.19	0.09	0.59	0.06	0.26	0.68
Atactic	0.30	0.18	0.30	0.12	0.06	0.04	0.45	0.45	0.10
Syndiotactic	0.48	0.15	0.24	0.07	0.05	0.01	0.60	0.35	0.05

a. calculated from tetrads

Table 4-6. Relative Tetrad and Calculated Triad Intensities from the Backbone Methylene Carbon Resonance of Poly(n-pentyl α-bromoacrylate).

Tacticity	Tetrads						Triads[a]		
	rrr	rmr	rrm	mmr	mrm	mmm	rr	mr	mm
Isotactic	0.01	0.02	0.07	0.17	0.08	0.65	0.04	0.22	0.74
Atactic	0.30	0.18	0.29	0.12	0.07	0.04	0.45	0.45	0.10
Syndiotactic	0.51	0.16	0.20	0.06	0.06	0.01	0.61	0.35	0.04

a. calculated from tetrads

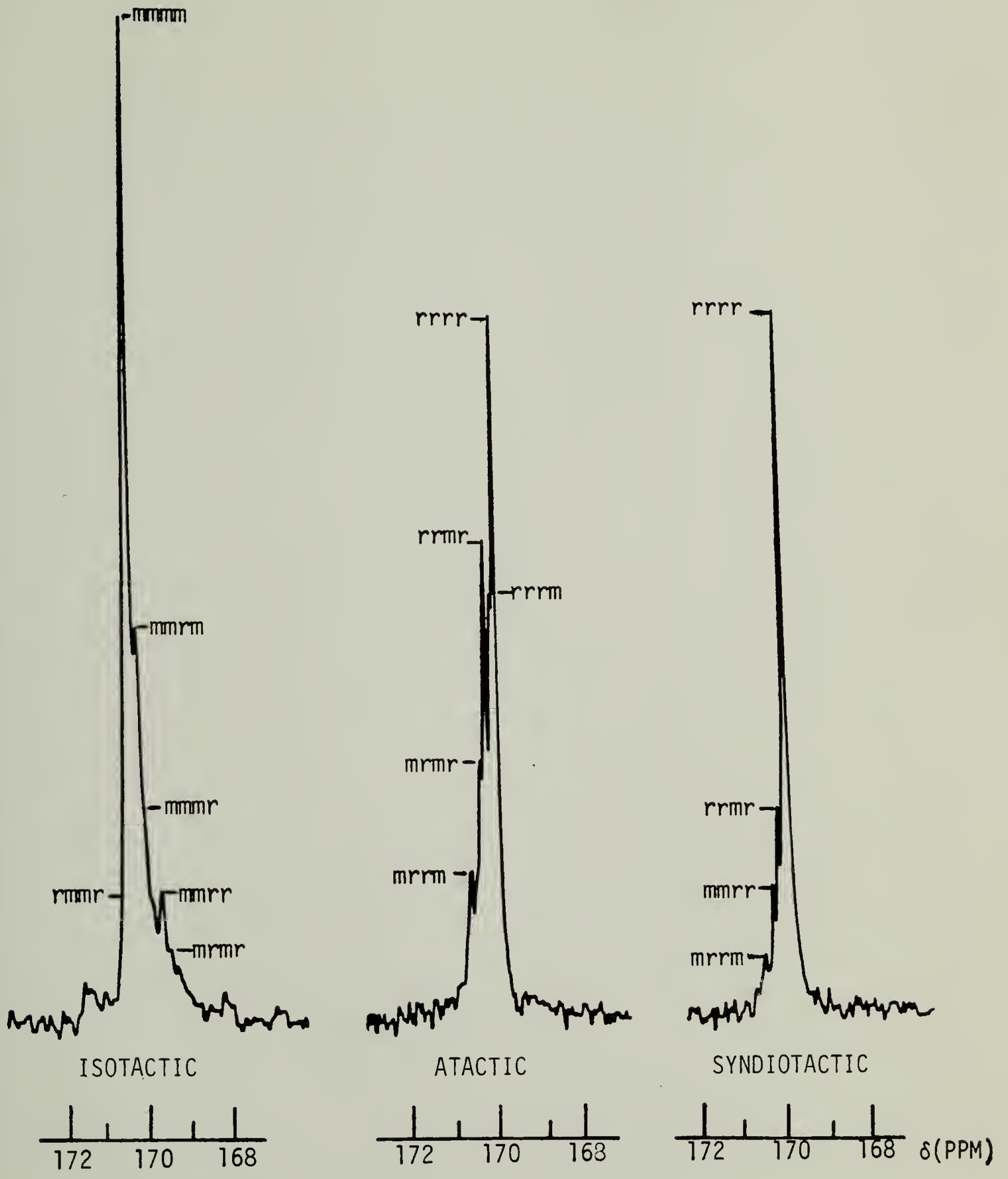
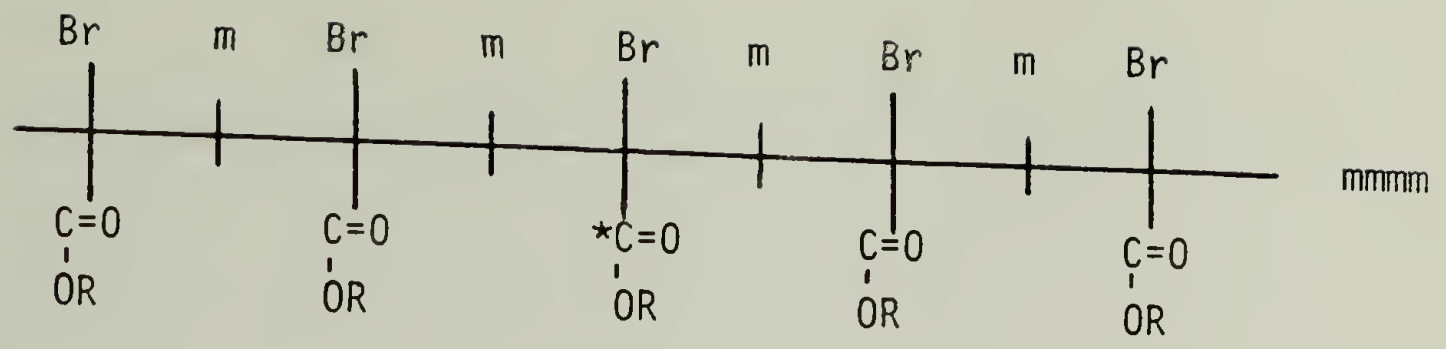


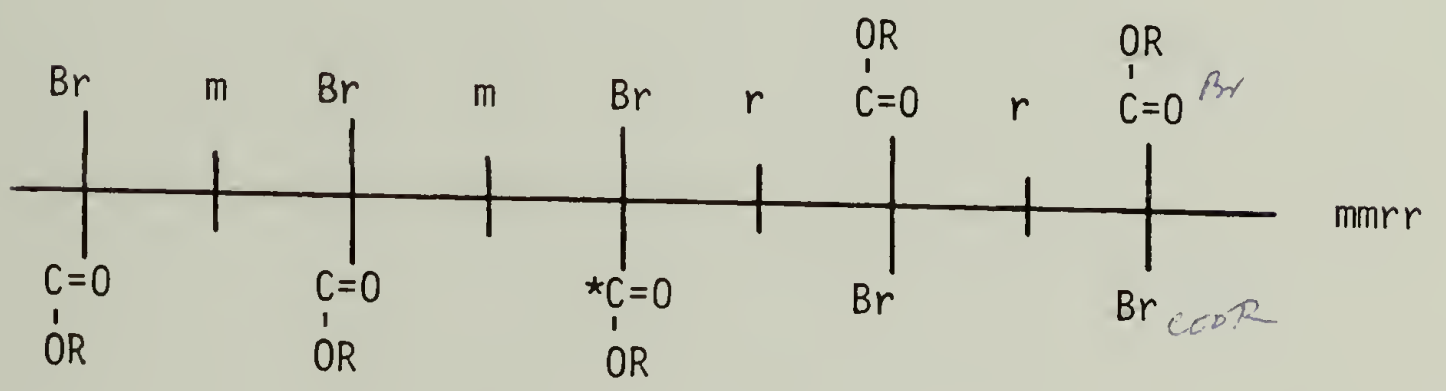
Figure 4-6. The Carbonyl Carbon Resonance of Poly(methyl-α-bromoacrylate) in ppm Relative to TMS

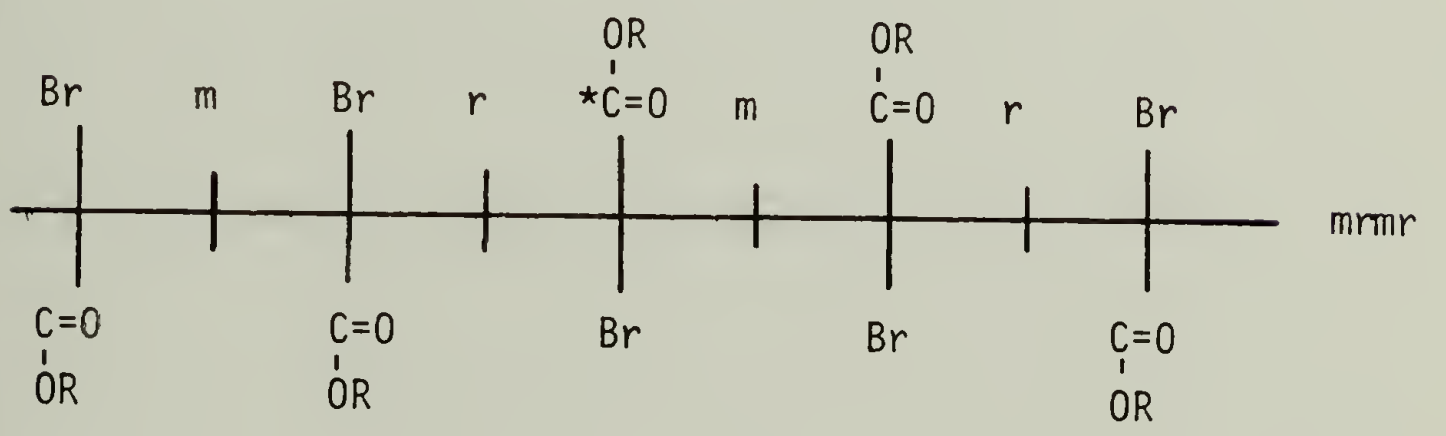
tactic form is easily seen in these figures (see also Figures 4-19 through 4-24). For instance, the isotactic sample had a peak maximum at the extreme left of the absorption region while the syndiotactic sample had the maximum at the extreme right of the absorption region. This observation was further demonstrated by Figure 4-7 where the ^{13}C spectrum was obtained from a sample containing roughly equal amounts of the isotactic and syndiotactic polymers. Immediately noticeable was the resolution of a minimum of six peaks and therefore, resolution into pentads was likely. Assuming pentad splitting, the peaks at the extreme left and right of the spectra were assigned with a reasonable degree of certainty to mmmm and rrrr units, respectively. The remaining eight theoretically expected peaks were then assigned within these two extremes. Four representative pentads are shown in Figure 4-8 where the carbonyl carbon bearing the asterisk is the resonance under observation. The mrmr and mmrr structures depict the two possible heterotactic pentads.

The process of assigning the remaining eight pentad peaks was conducted in a similar manner to that applied for assigning the tetrad peaks. In other words, the next strongest peak in the isotactic resonance was assigned to the mmrm peak followed by the mmmr peak to the third strongest. The identical principle was used in assigning the rrmr and rrrm peaks. These assignments were aided by the relative intensity of each pentad as calculated from the tetrad values of the backbone methylene carbon resonance. For the atactic and syndiotactic samples, Bernoullian statistics were used while first order Markovian statistics were used for the isotactic polymers. These calculations

Figure 4-7. The Carbonyl Carbon Resonance of Roughly Equal Amounts of Isotactic and Syndiotactic Poly(methyl-α-bromoacrylate) in ppm Relative to TMS







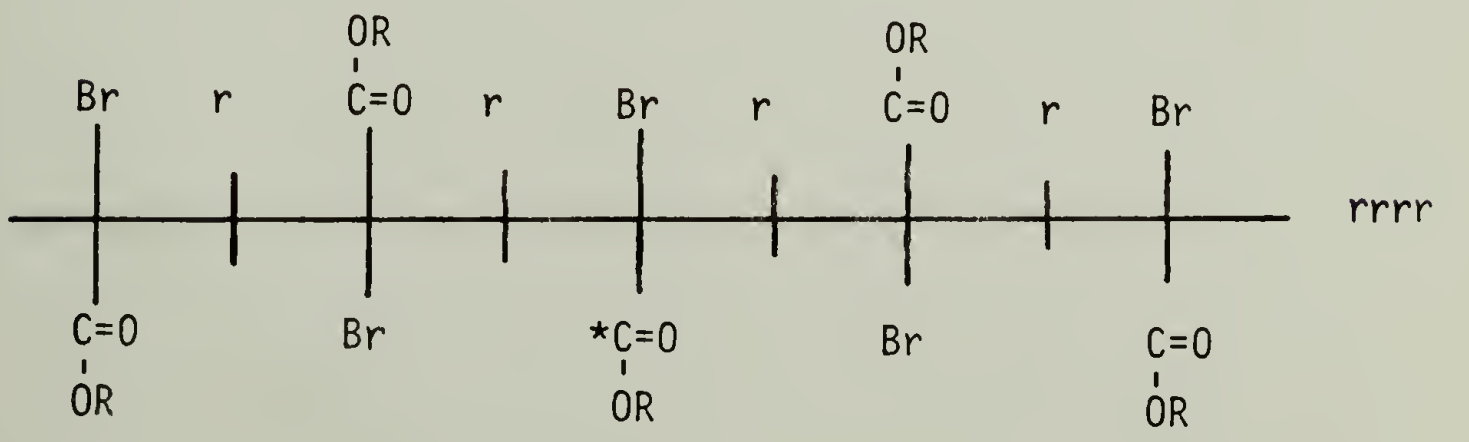


Figure 4-8. Four Representative Pentad Structures for the Poly(alkyl α-bromoacrylate)s

are not presented but similar calculations are listed in Table 4-28 for the isotactic polymers.

Complete pentad assignments were possible for poly(methyl α-bromoacrylate), Figures 4-6 and 4-7, because the three samples available for analysis contained a wide variety of tacticities. By proper combination of the three polymer spectra, the chemical shifts for all ten pentad peaks were identified.

Pentads, like tetrads, are also subject to necessary relationships which must be obeyed in order for the assignments to be correct. In addition to the requirement that the sum of all the pentads must equal one, two additional relationships must also be satisfied:

$$mmmr + 2(rmmr) = mmrm + mmrr \qquad (5)$$

$$rrrm + 2(mrrm) = rrmr + mmrr \qquad (6)$$

The fact that these equalities were almost always obeyed to within 5% for the methyl ester verifies the correctness of these pentad assignments. The order of the peak assignments as a function of increasing field strength were determined to be:

mmmm < mmrm < mmmr < rmmr < mrrm < mmrr < mrmr < rrmr < rrrm < rrrr

The relative intensities and peak chemical shifts for these peaks are listed in Table 4-7.

Figures 4-9 through 4-13 contain the carbonyl carbon resonance for the isotactic, atactic and syndiotactic samples of the ethyl through n-pentyl esters. The assignments for these esters were found to be identical with each other although, they differed slightly from those of the previously discussed methyl ester. Fortunately, the chemical shifts between the pentad peaks were slightly larger for these esters

Table 4-7. Relative Pentad Intensities and Peak Chemical Shifts from the Carbonyl Carbon Resonance of Poly(methyl α-bromoacrylate).

Pentads	Chemical shift, ppm[a]	Relative Intensities		
		Isotactic	Atactic	Syndiotactic
rrrr	168.99	0.01	0.27	0.50
rrrm	169.15	0.02	0.14	0.12
rmmr	169.32	0.02	0.19	0.17
mrmr	169.41	0.03	0.13	0.08
mmrr	169.53	0.05	0.10	0.05
mrrm	169.70	0.03	0.06	0.04
rmmr	169.86	0.05	0.06	0.02
mmmr	170.00	0.09	0.02	0.01
mmrm	170.30	0.14	0.02	0.01
mmmm	170.52	0.56	0.01	-

a. relative to TMS

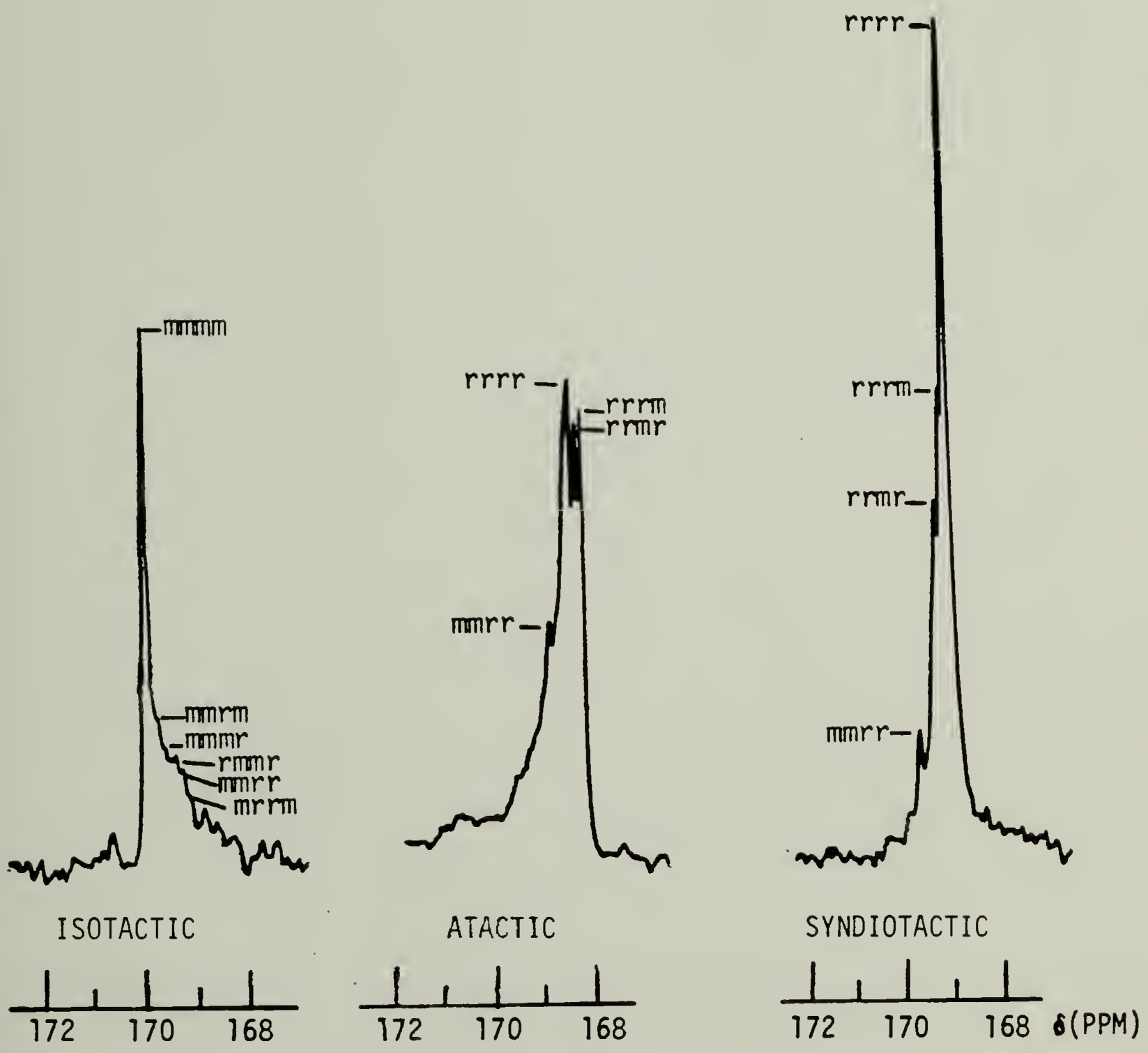


Figure 4-9. The Carbonyl Carbon Resonance of Poly(ethyl-α-bromoacrylate) in ppm Relative to TMS

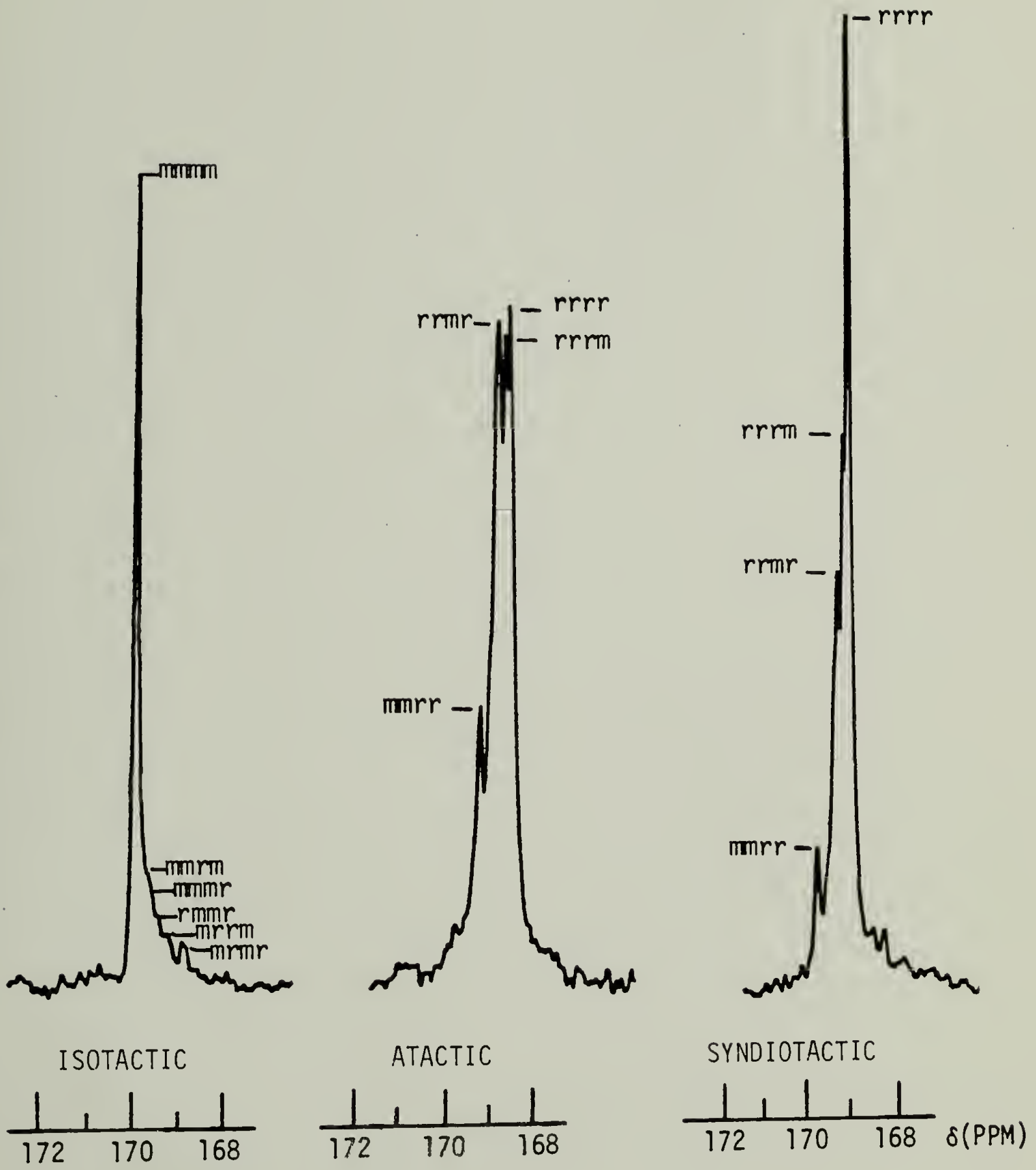


Figure 4-10. The Carbonyl Carbon Resonance of Poly(n-propyl-α-bromoacrylate) in ppm relative to TMS

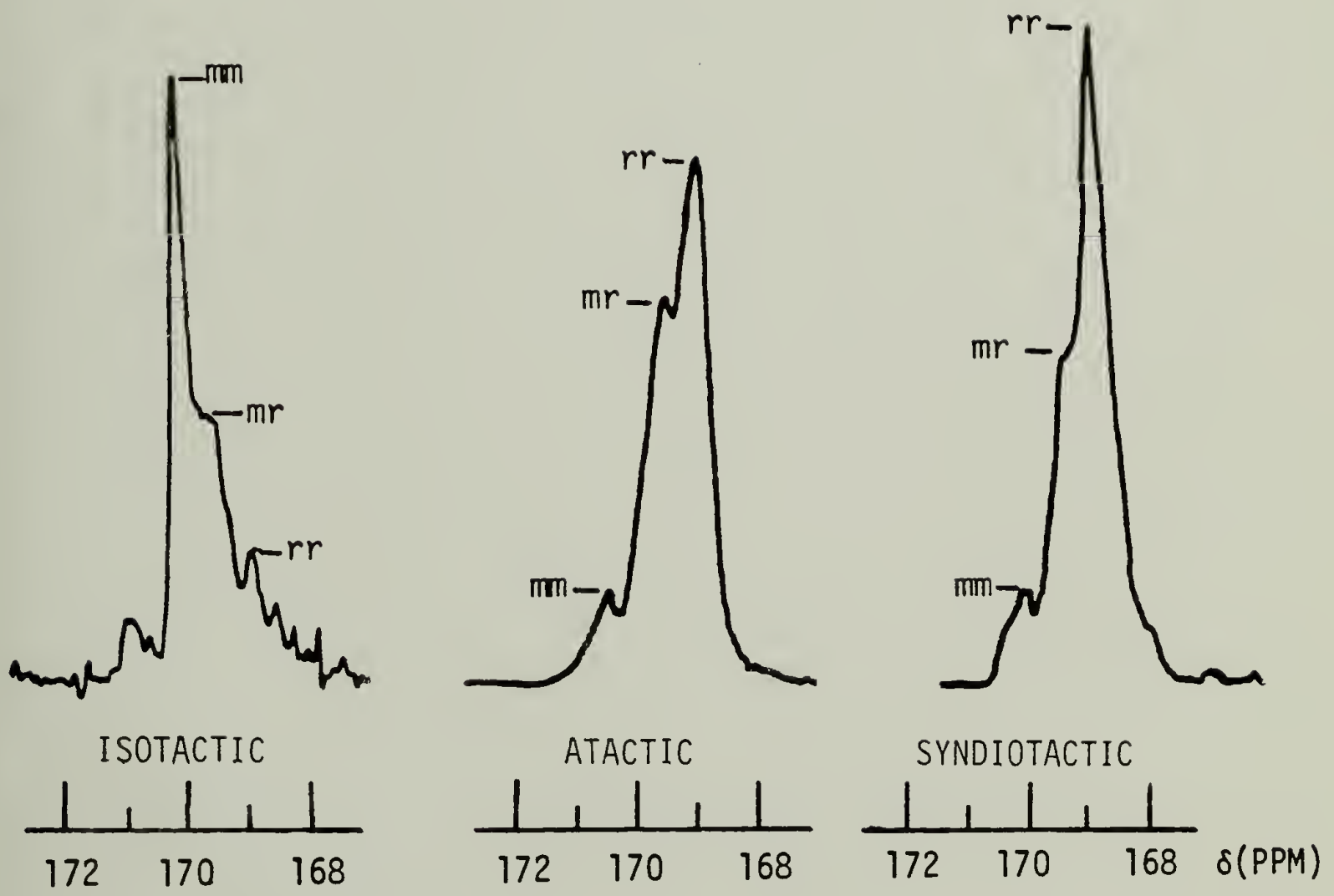


Figure 4-11. The Carbonyl Carbon Resonance of Poly(i-propyl-α-bromoacrylate) in ppm Relative to TMS

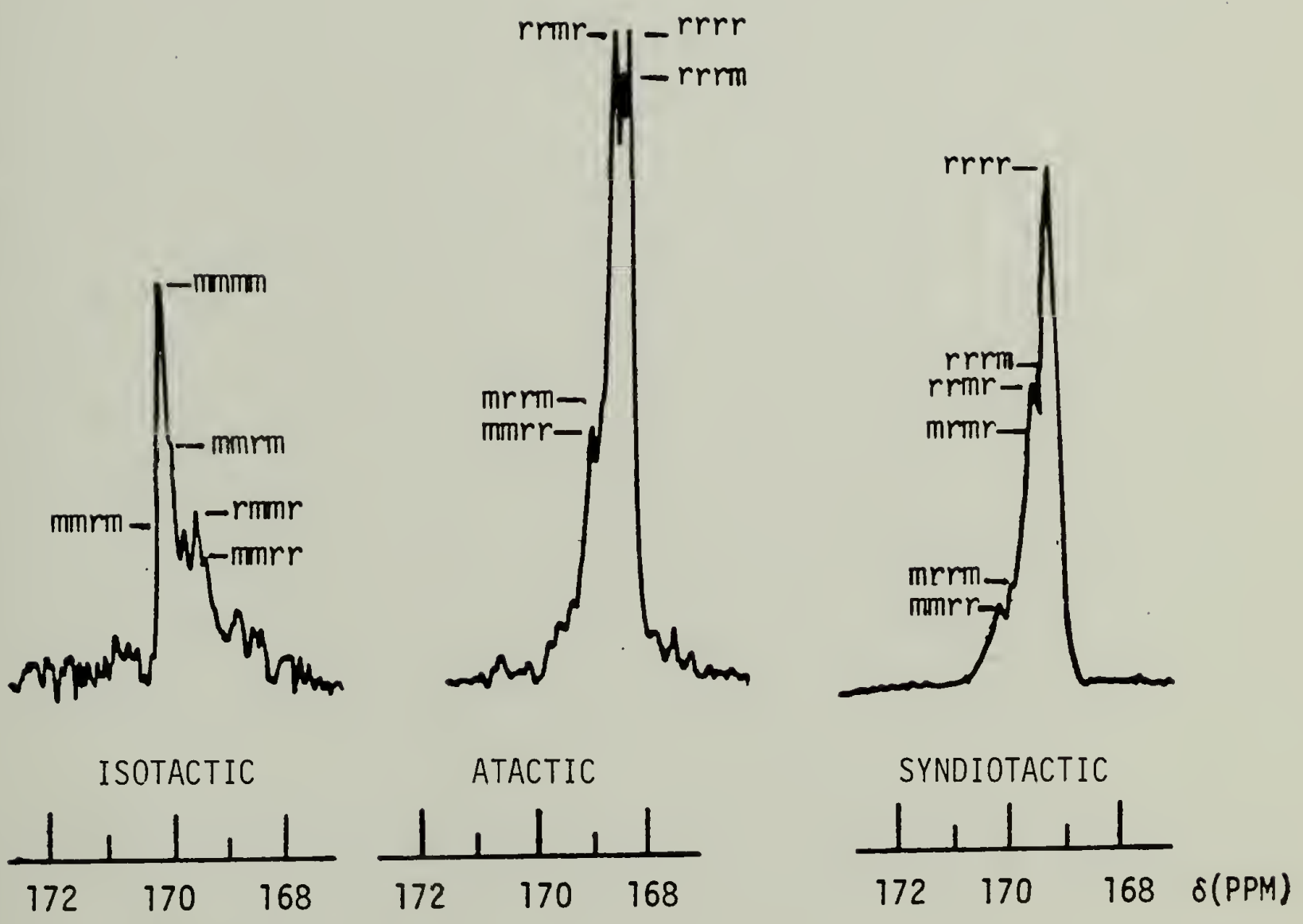


Figure 4-12. The Carbonyl Carbon Resonance of Poly(n-butyl-α-bromoacrylate) in ppm Relative to TMS

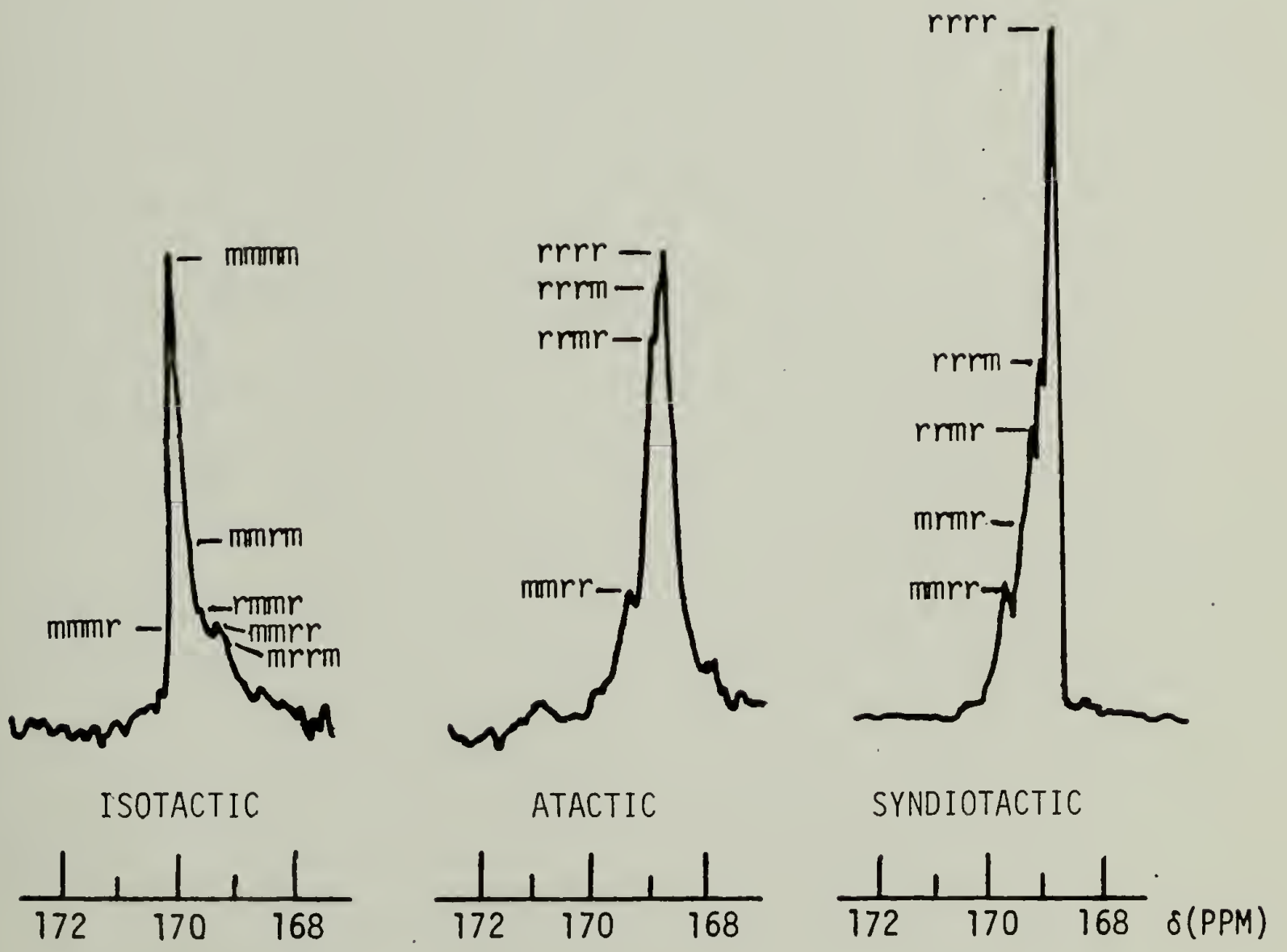


Figure 4-13. The Carbonyl Carbon Resonance of Poly(n-pentyl-α-bromoacrylate) in ppm Relative to TMS.

than for poly(methyl α-bromoacrylate) and therefore made their identification somewhat easier. In fact, all ten pentad peaks were clearly visible from the spectra of both isotactic poly(ethyl α-bromoacrylate), Figure 4-9 and isotactic poly(n-butyl α-bromoacrylate), Figure 4-12. In addition, these two samples were the least stereoregular of all the isotactic polymers synthesized and as a result contained higher concentrations of the syndiotactic rich units which assisted further in peak identification. The only difference in these peak assignments from the previous were that the mrrm and mmrr pentads were transposed. Accordingly, the peaks were assigned in the following order:

mmmm < mmrm < mmmr < rmmr < mmrr <

mrrm < mrmr < rrmr < rrrm < rrrr

with increasing field strength. These assignments obeyed equations (5) and (6) for the isotactic, atactic and syndiotactic samples of the ethyl, n-propyl, n-butyl and n-pentyl esters, again furnishing evidence for the validity of the assignments. The relative intensities and peak chemical shifts for these pentads are listed in Tables 4-7 through 4-11.

Due to the insufficient peak resolution for all of the i-propyl ester samples, the tacticity could be interpreted in terms of triads only. The result of this analysis is given in Table 4-12.

Resolution of the quaternary carbon resonance. Tacticity measured from the quaternary carbon resonance reflected the same tacticity, i.e., pentad, as measured by the carbonyl carbon resonance. For instance, in the four pentad structures depicted previously, the quaternary carbon was α to the carbonyl carbon and therefore was exposed to the same

Table 4-8. Relative Pentad Intensities and Peak Chemical Shifts from the Carbonyl Carbon Resonance of Poly(ethyl α-bromoacrylate).

Pentads	Chemical shift, ppm[a]	Relative Intensities		
		Isotactic	Atactic	Syndiotactic
rrrr	168.50	0.01	0.21	0.42
rrrm	168.66	0.02	0.14	0.15
rrmr	168.84	0.02	0.18	0.20
mrmr	169.32	0.03	0.12	0.09
mrrm	169.53	0.04	0.10	0.05
mmrr	169.71	0.08	0.09	0.05
rmmr	169.93	0.09	0.06	0.02
mmmr	170.17	0.08	0.04	0.01
mmrm	170.45	0.12	0.04	0.01
mmmm	170.60	0.51	0.02	-

a. relative to TMS

Table 4-9. Relative Pentad Intensities and Peak Chemical Shifts from the Carbonyl Carbon Resonance of Poly(n-propyl α-bromoacrylate).

Pentads	Chemical shift,ppm[a]	Relative Intensities		
		Isotactic	Atactic	Syndiotactic
rrrr	168.51	0.01	0.21	0.42
rrrm	168.67	0.01	0.17	0.16
rrmr	168.85	0.02	0.20	0.18
mrmr	169.01	0.03	0.14	0.10
mrrm	169.20	0.03	0.08	0.05
mmrr	169.48	0.04	0.07	0.05
rmmr	169.69	0.05	0.05	0.03
mmmr	169.92	0.07	0.04	0.01
mmrm	170.21	0.11	0.03	-
mmmm	170.40	0.63	0.01	-

a. relative to TMS

Table 4-10. Relative Pentad Intensities and Peak Chemical Shifts from the Carbonyl Carbon Resonance of Poly(n-butyl α-bromoacrylate).

Pentads	Chemical shift,ppm[a]	Relative Intensities		
		Isotactic	Atactic	Syndiotactic
rrrr	168.54	0.01	0.21	0.41
rrrm	168.69	0.02	0.15	0.15
rrmr	168.87	0.02	0.19	0.19
mrmr	169.48	0.04	0.14	0.09
mrrm	169.70	0.04	0.10	0.05
mmrr	170.03	0.07	0.09	0.05
rmmr	170.17	0.08	0.05	0.03
mmmr	170.27	0.07	0.03	0.02
mmrm	170.54	0.16	0.03	0.01
mmmm	170.73	0.49	0.01	-

a. relative to TMS

Table 4-11. Relative Pentad Intensities and Peak Chemical Shifts from the Carbonyl Carbon Resonance of Poly(n-pentyl α-bromoacrylate).

Pentads	Chemical shift,ppm[a]	Relative Intensities		
		Isotactic	Atactic	Syndiotactic
rrrr	168.53	-	0.22	0.46
rrrm	168.84	0.02	0.15	0.14
rrmr	169.15	0.02	0.18	0.19
mrmr	169.32	0.03	0.13	0.08
mrrm	169.58	0.05	0.10	0.04
mmrr	169.84	0.07	0.09	0.05
rmmr	170.16	0.06	0.05	0.02
mmmr	170.37	0.08	0.03	0.01
mmrm	170.65	0.12	0.03	0.01
mmmm	170.95	0.55	0.02	-

a. relative to TMS

Table 4-12. Relative Pentad Intensities and Peak Chemical Shifts from the Carbonyl Carbon Resonance of Poly(i-propyl α-bromoacrylate).

Pentad	Chemical shift, ppm[a]	Relative Intensities		
		Isotactic	Atactic	Syndiotactic
rrrr rrrm rrmr	168.95	0.10	0.46	0.60
mrmr mrrm mmrr rmmr	169.61	0.30	0.42	0.35
mmmr mmrm mmmm	170.52	0.60	0.12	0.05

a. relative to TMS

basic environment as the carbonyl carbon. Thus, it was anticipated that the pentad tacticities measured from two different carbon atoms could be coupled with the tetrad tacticity to serve as an internal check on tacticity and to determine the polymer configuration as accurately as possible.

The quaternary carbon resonance is exhibited in Figures 4-14 through 4-18 for the methyl, n-propyl, i-propyl, n-butyl, and n-pentyl esters, respectively. Determination of polymer tacticity was not possible from the quaternary carbon of poly(ethyl α-bromoacrylate) as a result of peak overlap from the methylene carbon of the ethyl ester group. Complete pentad assignments were not possible for most of the polymers in this investigation due to insufficient peak separation.

Best results were achieved with poly(methyl α-bromoacrylate) where all the pentad peaks were assigned for both the atactic and syndiotactic polymers. The peak intensities and their corresponding chemical shifts are presented in Table 4-13. In the case of the isotactic sample, the small chemical shift differences prohibited the assignment of each pentad peak. However, from the peak assignments of the atactic and syndiotactic samples, the observable peaks could be interpreted in terms of pentad tacticities. The collective relative intensities presented in Table 4-13 agree well with the pentad tacticities from the carbonyl carbon resonance of the same sample, Table 4-7. The order of the peak assignments with increasing magnetic field were determined to be:

rrrr < rrrm < rrmr < mrmr < mrrm <

rmmr < mmrr < mmmr < mmrm < mmmm

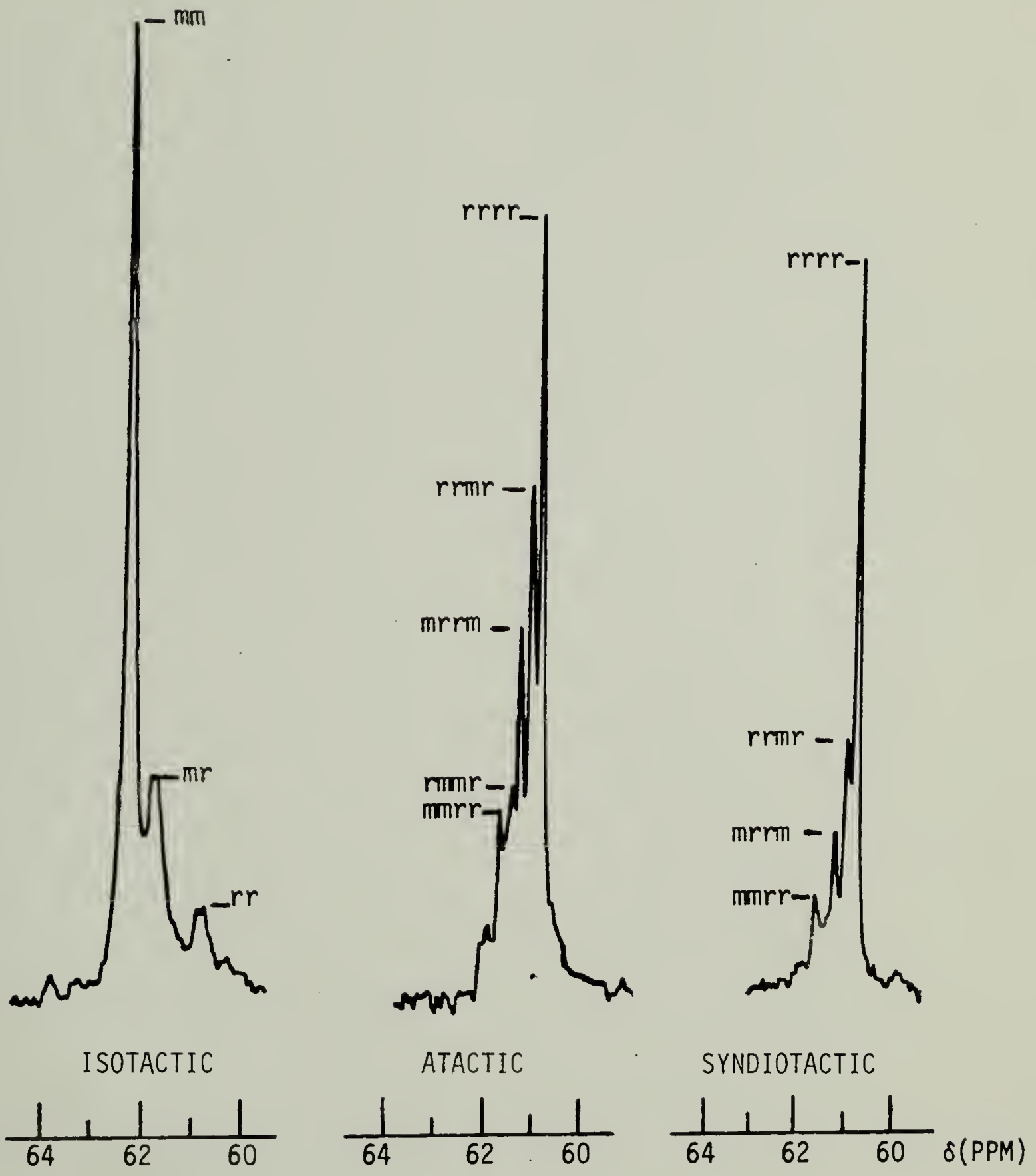


Figure 4-14. The Quaternary Carbon Resonance of Poly(methyl-α-bromoacrylate) in ppm Relative to TMS

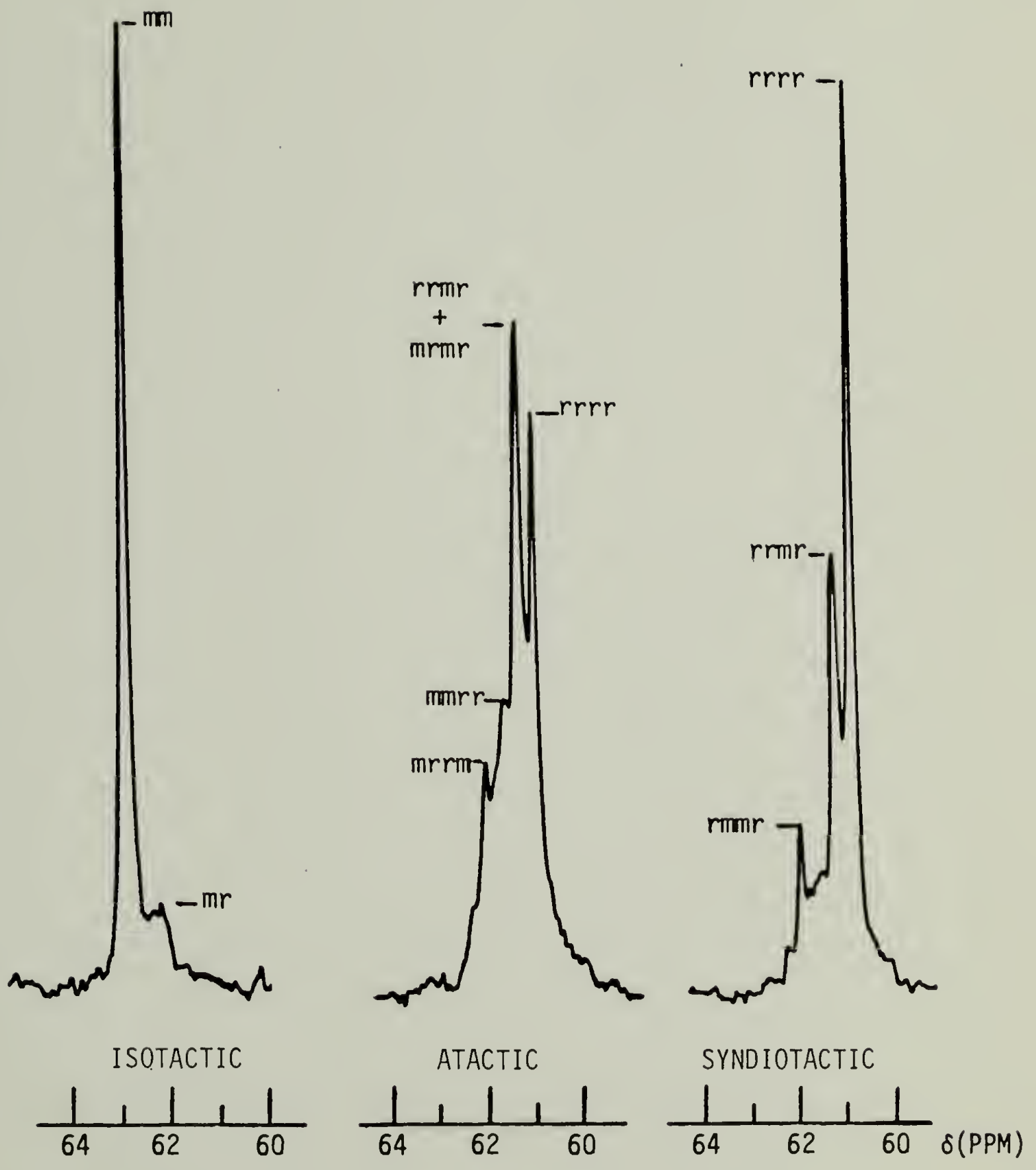


Figure 4-15. The Quaternary Carbon Resonance of Poly(n-propyl-α-bromoacrylate) in ppm Relative to TMS

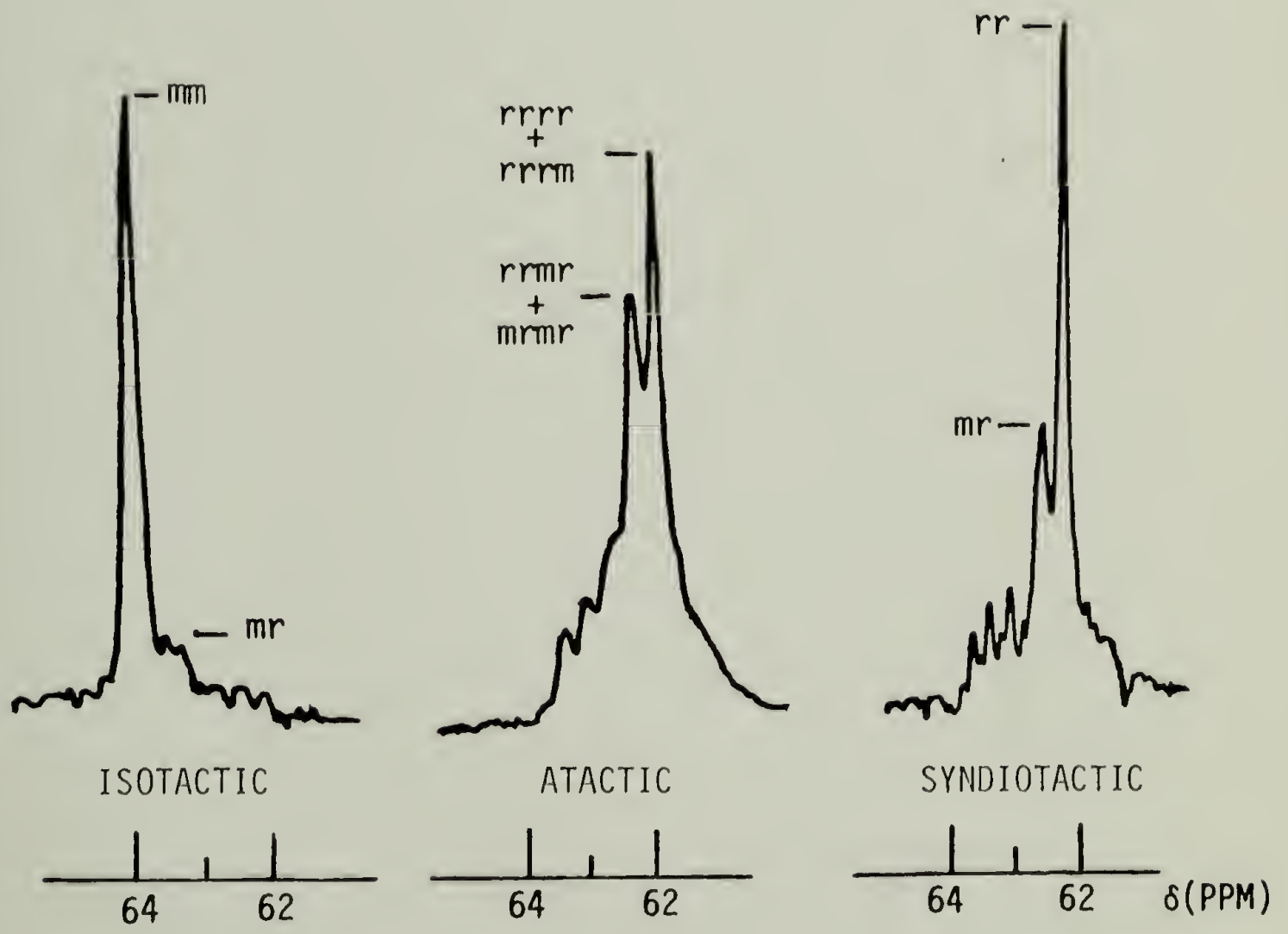


Figure 4-16. The Quaternary Carbon Resonance of Poly(i-propyl-α-bromoacrylate) in ppm Relative to TMS

Figure 4-17. The Quaternary Carbon Resonance of Poly(n-butyl-α-bromoacrylate) in ppm Relative to TMS

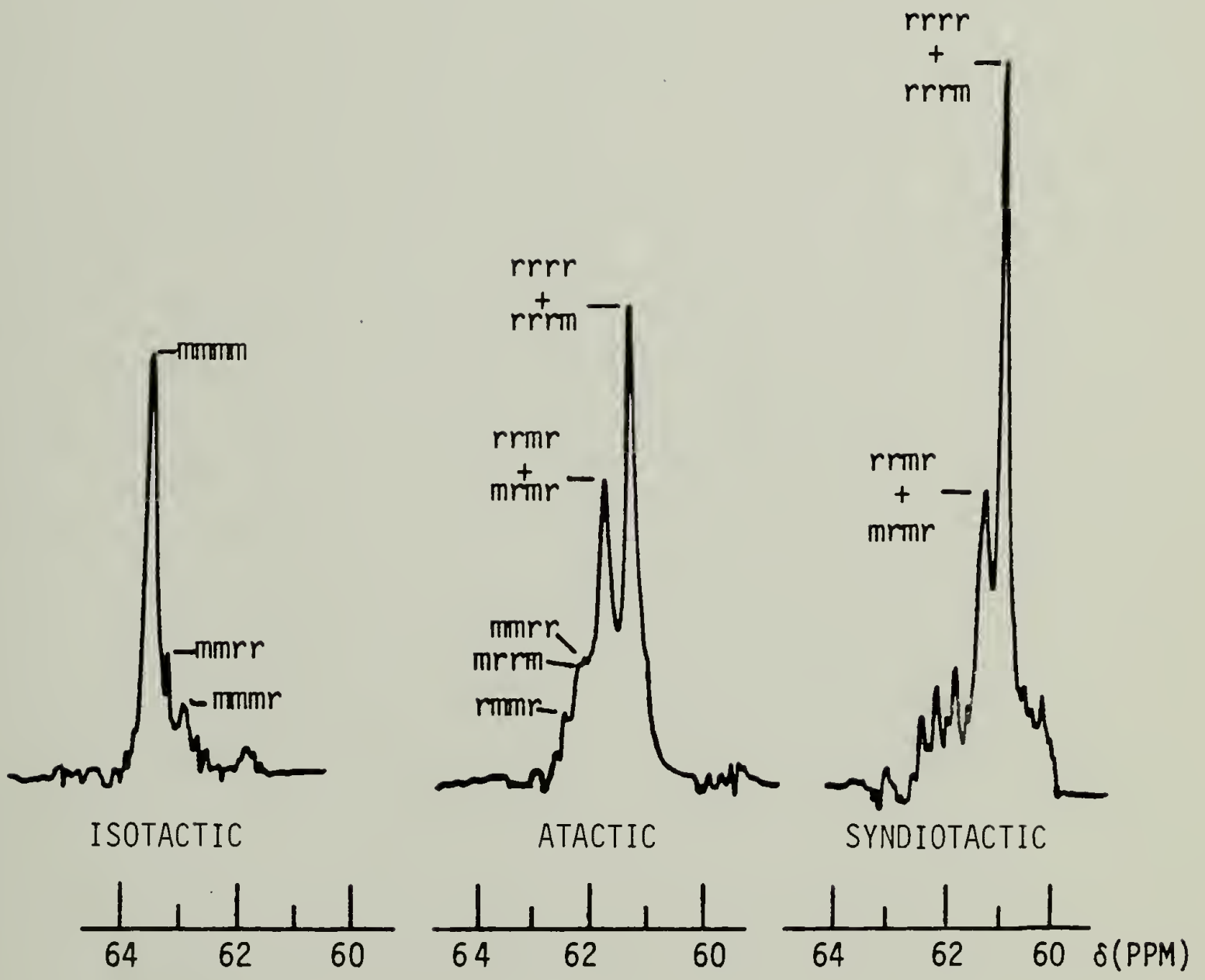


Figure 4-18. The Quaternary Carbon Resonance of Poly(n-pentyl-α-bromoacrylate) in ppm Relative to TMS

Table 4-13. Relative Pentad Intensities and Peak Chemical Shifts from the Quaternary Carbon Resonance for Poly(methyl α-bromoacrylate).

Pentads	Chemical shift, ppm[a]	Relative Intensities		
		Isotactic	Atactic	Syndiotactic
rrrr	60.85	-	0.29	0.46
rrrm	60.97	0.02	0.13	0.11
rrmr	61.15	0.03	0.18	0.15
mrmr	61.32	0.04	0.13	0.09
mrrm	61.50		0.08	0.05
rmmr	61.62	0.15	0.05	0.05
mmrr	61.80		0.07	0.06
mmmr	62.05		0.02	0.02
mmrm	62.20	0.76	0.03	0.01
mmmm	62.31		0.02	-

a. relative to TMS

and they satisfy equations (5) and (6) to within 5%. The order of these peaks are slightly different than the previous two sets.

Of the remaining esters, only the isotactic samples of poly(n-butyl α-bromoacrylate) and poly(n-pentyl α-bromoacrylate) could be assigned into all the ten pentad structures, Figures 4-17 and 4-18. The order of these assignments were again different than those of poly(methyl α-bromoacrylate) just given but were identical to those of the carbonyl carbon resonance for poly(methyl α-bromoacrylate) and therefore were:

rrrr < rrrm < rrmr < mrmr < mmrr <

mrrm < rmmr < mmmr < mmrm < mmmm

with increasing field strength. In the samples where complete assignments were not possible, the individual pentad peaks were consolidated into one and the collective tacticities calculated. The values calculated as such are listed in Tables 4-14 through 4-17 for the n-propyl, n-butyl, n-pentyl and i-propyl esters, respectively. Comparison of this tacticity data with the sum of the appropriate pentad tacticities from the carbonyl carbon resonance (Tables 4-9 through 4-12) reveals satisfactory agreement. This was taken as a confirmation of the pentad assignments from both the carbonyl and quaternary carbon resonances. Furthermore, it will be shown in the succeeding section that the tetrad tacticities calculated from the carbonyl carbon pentads agree well with the tetrads experimentally determined from the backbone methylene carbon resonance.

As with the carbonyl carbon resonance, the i-propyl ester could be interpreted only in terms of the triad structures shown in Table 4-17.

Table 4-14. Relative Pentad Intensities and Peak Chemical Shifts from the Quaternary Carbon Resonance for Poly(n-propyl α-bromoacrylate).

Pentads	Chemical shift,ppm[a]	Relative Intensities		
		Isotactic	Atactic	Syndiotactic
rrrr	61.20	-	0.23	0.40
rrrm	61.40	0.01	0.14	0.13
rrmr	61.72	0.01	0.28	0.19
mrmr	62.01	0.03		0.09
mmrr	62.23	0.05	0.11	0.05
mrrm	62.46	0.05	0.09	0.04
rmmr	62.70	0.04	0.08	0.04
mmmr	62.91	0.81	0.07	0.06
mmrm	63.11			
mmmm	63.23			

a. relative to TMS

Table 4-15. Relative Pentad Intensities and Peak Chemical Shifts from the Quaternary Carbon Resonance for Poly(n-butyl α-bromoacrylate).

Pentads	Chemical shift, ppm[a]	Relative Intensities		
		Isotactic	Atactic	Syndiotactic
rrrr, rrrm	61.15	0.03	0.29	0.55
rrmr	61.68	0.03	0.31	0.24
mrmr	62.08	0.04		
mmrr	62.35	0.05	0.12	0.14
mrrm	62.66	0.07	0.11	
rmmr	62.83	0.07	0.08	
mmmr	63.05	0.12	0.09	0.07
mmrm	63.16	0.17		
mmmm	63.27	0.42		

a. relative to TMS

Table 4-16. Relative Pentad Intensities and Peak Chemical Shifts from the Quaternary Carbon Resonance for Poly(n-pentyl α-bromoacrylate).

Pentads	Chemical shift, ppm[a]	Relative Intensities		
		Isotactic	Atactic	Syndiotactic
rrrr	61.16	0.01	0.35	0.56
rrrm	61.30	0.02		
rrmr	61.63	0.02	0.30	0.26
mrmr	61.90	0.03		
mmrr	62.20	0.04	0.11	
mrrm	62.50	0.04	0.10	0.12
rmmr	62.78	0.05	0.07	
mmmr	63.05	0.08		
mmrm	63.26	0.12	0.07	0.06
mmmm	63.46	0.59		

a. relative to TMS

Rable 4-17. Relative Pentad Intensities and Peak Chemical Shifts from the Quaternary Carbon Resonance for Poly(i-propyl α-bromoacrylate).

Pentads	Chemical shift,ppm[a]	Relative Intensities		
		Isotactic	Atactic	Syndiotactic
rrrr rrrm rrmr	62.04	0.10	0.60	-
mrmr mmrr mrrm rmmr	62.90	0.32	0.33	-
mmmr mmrm mmmm	63.95	0.58	0.07	-

a. relative to TMS

These tacticities, however, agree well with those in Table 4-12 for the carbonyl carbon resonance of this polymer.

Discussion

Tetrad tacticity. The validity of the pentad assignments from the carbonyl carbon resonance was fairly well substantiated by the fact the equations (5) and (6) were satisfied to within 5% in almost all cases. These assignments also agreed well with the pentad assignments from the quaternary carbon resonance. Nevertheless, it was felt that if the tetrad tacticity calculated from the pentads was comparable to the tetrads measured experimentally from the backbone methylene carbon resonance, an additional confirmation of the pentad assignments would be possible.

The equations used for the calculation of the tetrads from the pentads are listed below[17]:

$$mmm = mmmm + 1/2\ mmmr$$

$$mmr = mmmr + 2(rmmr) = mmrm + mmrr$$

$$rmr = 1/2(mrmr) + 1/2(rrmr)$$

$$mrm = 1/2(mrmr) + 1/2(mmrm)$$

$$rrm = rrrm + 2(mrrm) = rrmr + mmrr$$

$$rrr = rrrr + 1/2\ rrrm$$

where the dual equalities given for the mmr and rrm equations are the necessary requirements for pentads as was previously pointed out. The results of these calculations are shown in Tables 4-18 through 4-21 for the ethyl, n-propyl, n-butyl and n-pentyl esters, respectively.

Table 4-18. Comparison of Experimentally Determined Tetrads with Those Calculated from Pentads for Poly(ethyl α-bromoacrylate).

	Experimental[a]			Calculated from Pentads[b]		
Tetrads	Isotactic	Atactic	Syndiotactic	Isotactic	Atactic	Syndiotactic
rrr	0.04	0.30	0.52	0.03	0.28	0.50
rmr	0.04	0.16	0.14	0.04	0.15	0.15
rrm	0.06	0.28	0.23	0.08	0.30	0.25
mmr	0.17	0.14	0.05	0.21	0.15	0.05
mrm	0.09	0.08	0.04	0.09	0.08	0.04
mmm	0.60	0.04	0.02	0.55	0.04	0.01

a. from backbone methylene carbon resonance
b. from carbonyl carbon resonance

Table 4-19. Comparison of Experimentally Determined Tetrads with Those Calculated from Pentads for Poly(n-propyl α-bromoacrylate).

	Experimental[a]			Calculated from Pentads[b]		
Tetrads	Isotactic	Atactic	Syndiotactic	Isotactic	Atactic	Syndiotactic
rrr	0.02	0.29	0.49	0.03	0.29	0.50
rmr	0.02	0.17	0.16	0.03	0.16	0.13
rrm	0.05	0.27	0.24	0.06	0.30	0.25
mmr	0.15	0.13	0.05	0.14	0.13	0.06
mrm	0.06	0.09	0.04	0.07	0.09	0.05
mmm	0.70	0.05	0.02	0.67	0.03	0.01

a. from backbone methylene carbon resonance
b. from carbonyl carbon resonance

Table 4-20. Comparison of Experimentally Determined Tetrads with Those Calculated from Pentads for Poly(n-butyl α-bromoacrylate).

	Experimental[a]			Calculated from Pentads[b]		
Tetrads	Isotactic	Atactic	Syndiotactic	Isotactic	Atactic	Syndiotactic
rrr	0.02	0.30	0.48	0.03	0.29	0.49
rmr	0.03	0.18	0.15	0.04	0.16	0.14
rrm	0.08	0.30	0.24	0.09	0.30	0.24
mmr	0.19	0.12	0.07	0.21	0.13	0.07
mrm	0.09	0.06	0.05	0.10	0.08	0.05
mmm	0.59	0.04	0.01	0.53	0.04	0.01

a. from backbone methylene carbon resonance
b. from carbonyl carbon resonance

Table 4-21. Comparison of Experimentally Determined Tetrads with Those Calculated from Pentads for Poly(n-pentyl α-bromoacrylate).

	Experimental[a]			Calculated from Pentads[b]		
Tetrads	Isotactic	Atactic	Syndiotactic	Isotactic	Atactic	Syndiotactic
rrr	0.01	0.30	0.51	0.03	0.30	0.53
rmr	0.02	0.18	0.16	0.03	0.16	0.14
rrm	0.07	0.29	0.20	0.09	0.31	0.22
mrm	0.17	0.12	0.06	0.17	0.13	0.05
mmr	0.08	0.07	0.06	0.08	0.06	0.05
mmm	0.65	0.04	0.01	0.60	0.04	0.01

a. from backbone methylene carbon resonance
b. from carbonyl carbon resonance

Tetrad tacticity could not be determined from poly(methyl α-bromoacrylate) due to peak overlap and from poly(i-propyl α-bromoacrylate) because of insufficient peak resolution.

The agreement between the experimentally determined and calculated tetrads was excellent for the atactic and syndiotactic polymers. The deviation for all of the values between the two techniques were for the most part within the limits of experimental error. Both of these polymer types were synthesized by free radical polymerization reactions. The syndiotactic polymers were prepared at -40°C using ultraviolet light and benzoin as a photo-initiator while the atactic polymers were synthesized at 50°C employing decanoyl peroxide as the initiator.

The agreement for the isotactic polymers was not quite as good as the other two tactic forms. In general, the value of the mmm tetrad calculated from the pentads was up to 10% lower than that experimentally determined. This decrease was reflected by a similar increase in the mmr tetrad. The remaining four tetrads agreed exceptionally well from both techniques. The exact reason for this discrepancy was not known but since it occurred only with the isotactic samples, it is doubtful that it originated from the peak assignments. The tetrad peaks in the isotactic samples were less clearly defined than either of those in the atactic or syndiotactic samples and therefore their respective areas were more difficult to measure. This may have contributed, at least in part, to the discrepancy between the two peak intensities. The overall agreement between the two sets of tetrad data presented in Tables 4-18 through 4-21 served as a reasonable and satisfactory confirmation for the validity of the tetrad and pentad assignments.

Triad tacticity. Since the measurement of tetrad or pentad tacticity was not possible for all of the polymers in this investigation, the calculated triad tacticities were utilized to compare the stereoregularity of all the isotactic, atactic and syndiotactic samples. The calculated triad intensities are exhibited in Table 4-22 for the isotactic polymers, in Table 4-23 for the atactic polymers and in Table 4-24 for the syndiotactic polymers. The triad tacticities originating from the pentads of the carbonyl carbon resonance were calculated from the tetrad tacticity presented in Tables 4-18 through 4-21, except for the i-propyl ester where the triad tacticity was taken directly from Table 4-12. The equations relating triads and tetrads are the following[17]:

$$rr = mmm + 1/2\ mmr$$

$$mr = mmr + 2(rmr) = rrm + 2(mrm)$$

$$mm = rrr + 1/2\ rrm$$

First considering the isotactic samples, it was seen that the mm triad values ranged from 0.60 to 0.76 which indicated that all the samples were composed of predominately isotactic sequences. In only the i-propyl ester did the value of the rr triad reach 0.10. The low isotacticity of this ester could have resulted from the poor spectra obtained for this polymer. The poor solubility of this polymer in all solvents prevented the use of polymer solutions above 10% and consequently the ^{13}C spectra contained a substantial degree of baseline noise (Figure 4-16). Furthermore, the thermal instability of all the polymers prohibited the use of temperatures above 60°C to assist in dissolving the polymer.

Table 4-22. Triad Tacticities for the Isotactic Polymers Calculated from Tetrads and Pentads

		From Tetrads[a]			From Pentads[b]		
Ester	Sample	rr	mr	mm	rr	mr	mm
Methyl	3	--	--	--	0.06	0.26	0.68
Ethyl	14	0.08	0.24	0.68	0.07	0.27	0.66
n-Propyl	23	0.04	0.19	0.77	0.05	0.21	0.74
i-Propyl	31	0.08	0.28	0.64	0.10	0.30	0.60
n-Butyl	39	0.06	0.26	0.68	0.07	0.29	0.64
n-Pentyl	44	0.04	0.22	0.74	0.05	0.25	0.70

a. backbone methylene carbon resonance
b. carbonyl carbon resonance

Table 4-23. Triad Tacticities for the Atactic Polymers Calculated from Tetrads and Pentads.

		From Tetrads[a]			From Pentads[b]		
Ester	Sample	rr	mr	mm	rr	mr	mm
Methyl	4	--	--	--	0.46	0.44	0.10
Ethyl	16	0.44	0.45	0.11	0.43	0.46	0.11
n-Propyl	24	0.43	0.45	0.12	0.44	0.47	0.09
i-Propyl	32	0.43	0.46	0.11	0.46	0.43	0.11
n-Butyl	40	0.45	0.45	0.10	0.45	0.46	0.09
n-Pentyl	45	0.45	0.45	0.10	0.46	0.44	0.10

a. backbone methylene carbon resonance
b. carbonyl carbon resonance

Table 4-24. Triad Tacticities for Syndiotactic Polymers Calculated from Tetrads and Pentads.

		From Tetrads[a]			From Pentads[b]		
Ester	Sample	rr	mr	mm	rr	mr	mm
Methyl	8	--	--	--	0.66	0.31	0.03
Ethyl	22	0.64	0.32	0.04	0.64	0.33	0.03
n-Propyl	30	0.61	0.35	0.04	0.62	0.34	0.04
i-Propyl	36	0.58	0.36	0.06	0.60	0.35	0.05
n-Butyl	43	0.60	0.35	0.05	0.61	0.35	0.04
n-Pentyl	47	0.61	0.35	0.04	0.64	0.33	0.03

a. backbone methylene carbon resonance
b. carbonyl carbon resonance

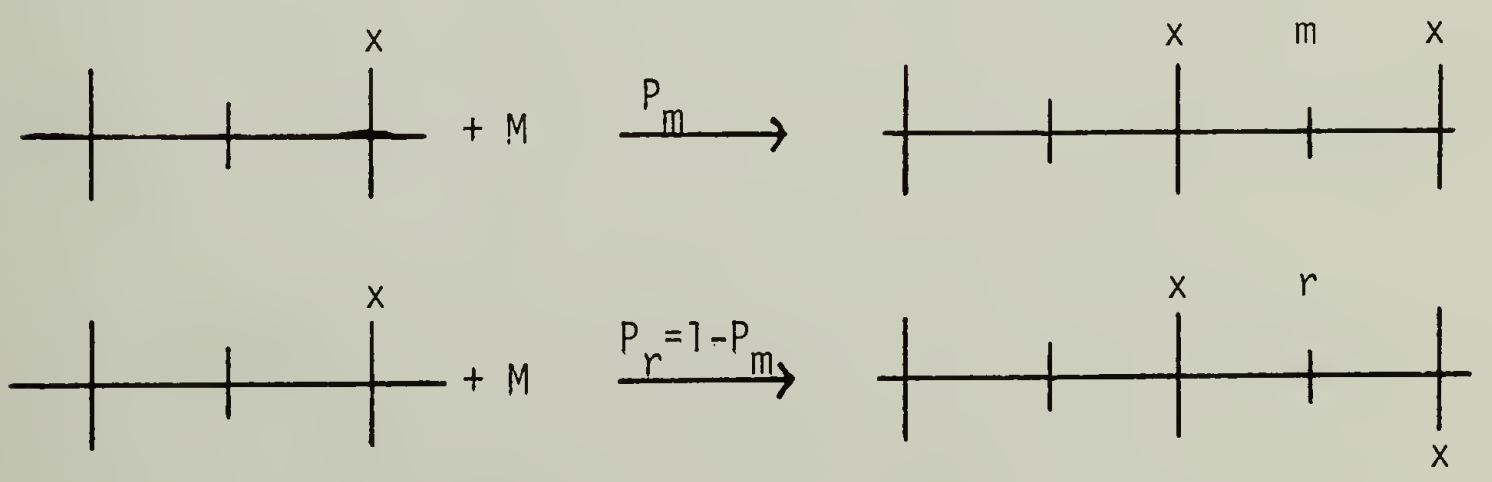
The atactic polymers displayed a fairly high degree of syndiotactic triads, about 0.45, for all of the esters. The relatively low percentage of the isotactic triad units compared to the syndiotactic triad units illustrated the difference in activation energy required for an isotactic versus syndiotactic placement. The propagation reaction involved in an isotactic unit required slightly more activation energy than in the corresponding syndiotactic propagation step. At the polymerization temperature of 50°C, the higher energy requirement of an isotactic placement was not satisfied and hence a predominately syndiotactic polymer resulted. The lower energy requirement for a syndiotactic placement is adequately explained by the lesser degree of steric interaction that arises from the bulky side groups in the syndiotactic configuration as compared to the corresponding isotactic configuration. This effect was more dramatic at the very low polymerization temperatures employed in the preparation of the syndiotactic polymers.

An inspection of Table 4-24 for the syndiotactic polymers revealed that the rr tacticities were between 0.58 and 0.66 and that all of the mm tacticities were below 0.06. Thus, a decrease in the polymerization temperature from 50 to -40°C resulted in a 20% increase in the syndiotactic content on a triad basis. At this low temperature, insufficient energy (heat) was available in the system to promote even a moderate degree of isotactic units. It is somewhat surprising that the longer esters did not have a higher syndiotactic content since they could be expected to contain an increased degree of steric repulsion in the isotactic configuration. It is conceivable that either experimental error in measuring the tacticity or fluctuations in the polymerization

temperature concealed this effect. In any event, the influence of ester group size on tacticity would be expected to be small. The tacticity values measured for these polymers were comparable to those of a series of poly(alkyl α-chloroacrylate)s synthesized under similar conditions[9].

Polymerization mechanism. The analysis of the configurational sequence statistics of polymers usually provides valuable information concerning the propagation mechanism of the polymerization process. Depending on the nature of the propagation mechanism, there are three basic distributions of the tactic sequences which can result and they are formed as a consequence of either block, alternation or random placements. In this brief analysis, four different statistical models will be considered: the Bernoullian, the first and second order Markovian and the Coleman-Fox.

The simplest type of sequence statistics result from building a chain by Bernoulli-trial where all the tactic sequences are generated from only one probability, P_m (or $P_r=1-P_m$) where P_m represents the random probability for the formation of an m dyad and P_r represents the random probability for the occurrence of an r dyad, as follows:



The most important feature of this propagation model is that the monomer (M) placement is completely independent of the stereochemistry of the propagating chain end. The configurational statistics of most vinyl polymers synthesized with free radical initiators have been found to follow this propagation model while similar polymers prepared by anionic initiators did not[17]. The following equations for triad, tetrad, and pentad tacticity demonstrate that all the tactic sequences can be built from this one probability, P_m[17]:

$$mm = P_m^2 \qquad mmmm = P_m^4$$

$$mr = 2P_m(1-P_m) \qquad mmmr = 2P_m^3(1-P_m)$$

$$rr = (1-P_m)^2 \qquad mmrm = 2P_m^3(1-P_m)$$

$$mmrr = 2P_m^2(1-P_m)^2$$

$$mmm = P_m^3 \qquad mrmr = 2P_m^2(1-P_m)^2$$

$$mmr = 2P_m^2(1-P_m) \qquad mrrm = P_m^2(1-P_m)^2$$

$$mrm = P_m^2(1-P_m) \qquad rmmr = P_m^2(1-P_m)^2$$

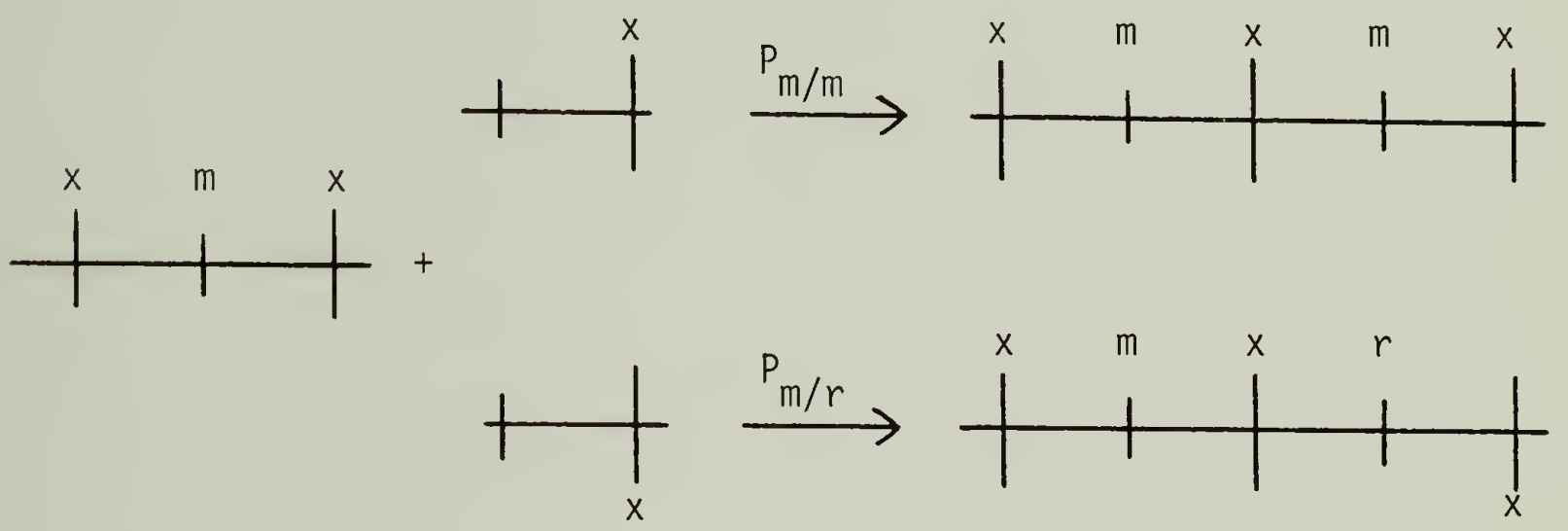
$$rmr = P_m(1-P_m)^2 \qquad rrmr = 2P_m(1-P_m)^3$$

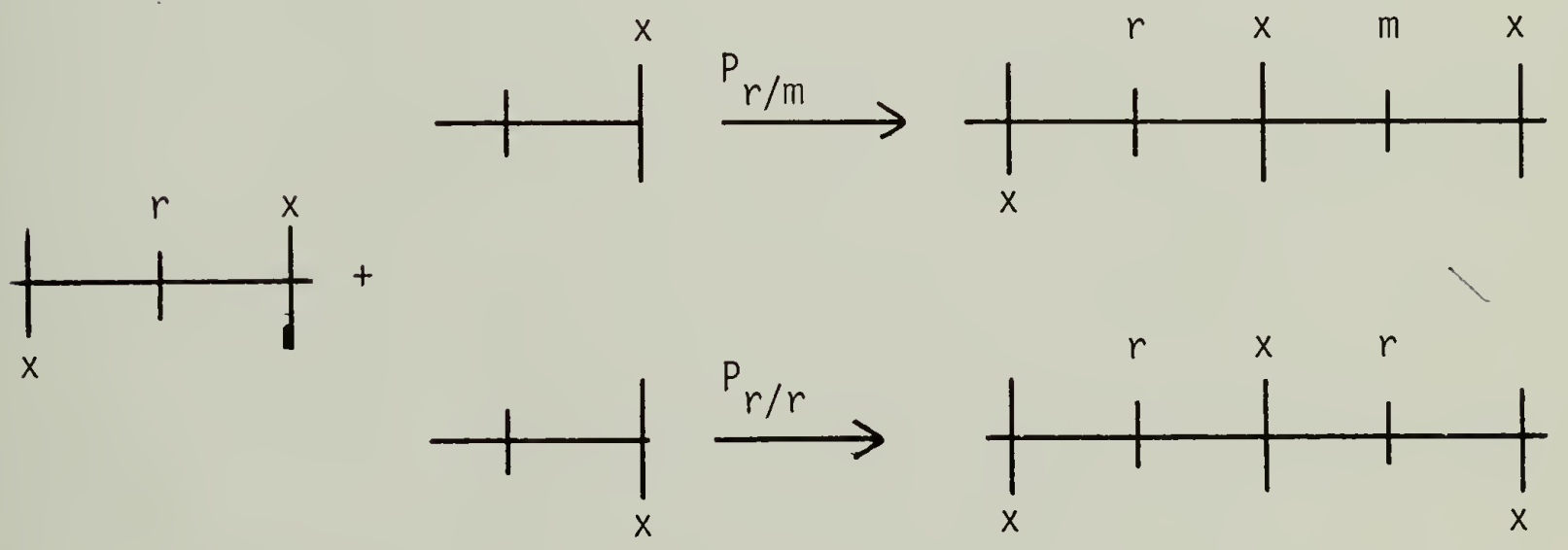
$$rrm = 2P_m(1-P_m)^2 \qquad rrrm = 2P_m(1-P_m)^3$$

$$rrr = (1-P_m)^3 \qquad rrrr = (1-P_m)^4$$

Many polymers synthesized by anionic means did not obey Bernoullian statistics but were found to follow much more closely with either first

or second order Markovian propagation statistics. A first-order Markov sequence is created when the propagation step of each adding monomer is influenced by the stereochemistry of the propagating chain end which, of course, may be r or m. Accordingly, there are four probabilities that characterize the addition process and are as follows:





The designation $P_{m/r}$ represents the probability that an r placement occurs to a growing chain end carrying an m unit. Thus, the first subscript corresponds to the configuration of the terminal unit on the chain while the second subscript refers to the placement of the incoming monomer unit. It is important to point out that the opposite convention has also been used to some extent. Since the following two conservative relationships are required:

$$P_{m/m} + P_{m/r} = 1$$

$$P_{r/r} + P_{r/m} = 1$$

there exist only two independent probabilities. We will consider them as $P_{m/r}$ and $P_{r/m}$.

As will be discussed later in this section, the values of these conditional probabilities will be employed to characterize the propagation process. These two probabilities are represented by the following two equations where the relationships in brackets are valid:

$$P_{m/r} = \frac{mr}{2(mm)\ mr} \quad [=(1-P_m)]$$

$$P_{r/m} = \frac{mr}{2(rr)\ mr} \quad [=P_m)$$

only for Bernoullian statistics and in that case, $P_{m/r} + P_{r/m} = 1$. If the triad, tetrad and pentad sequences are given in terms of $P_{m/r}$ and $P_{r/m}$, the following relationships result:

$$mm = \frac{(1-P_{m/r})P_{r/m}}{P_{m/r} + P_{r/m}}$$

$$mr = \frac{2P_{m/r}P_{r/m}}{P_{m/r} + P_{r/m}}$$

$$rr = \frac{(1-P_{r/m})P_{r/m}}{P_{m/r} + P_{r/m}}$$

$$mmm = \frac{(1-P_{m/r})^2 P_{r/m}}{P_{m/r} + P_{r/m}} \qquad \left[= \frac{(mm)^2}{m} \right]$$

$$mmr = \frac{2P_{m/r}(1-P_{m/r})P_{r/m}}{P_{m/r} + P_{r/m}} \qquad \left[= \frac{(mm)(mr)}{m} \right]$$

$$mrm = \frac{P_{m/r} P^2_{r/m}}{P_{m/r} + P_{r/m}} \qquad \left[= \frac{(mr)^2}{4r} \right]$$

$$rmr = \frac{P^2_{m/r}P_{r/m}}{P_{m/r} + P_{r/m}} \qquad \left[= \frac{(mr)^2}{4m} \right]$$

$$rrm = \frac{2P_{m/r}P_{r/m}(1-P_{r/m})}{P_{m/r} + P_{r/m}} \qquad \left[= \frac{(mr)(rr)}{m} \right]$$

$$rrr = \frac{P_{m/r}(1-P_{r/m})^2}{P_{m/r} + P_{r/m}} \qquad \left[= \frac{(rr)^2}{r} \right]$$

$$mmmm = \frac{P_{r/m}(1-P_{m/r})^3}{D} \quad \left[= \frac{(mmm)^2}{mm} \right]$$

$$mmmr = \frac{2P_{m/r}P_{r/m}(1-P_{m/r})^2}{D} \quad \left[= \frac{(mmm)(mmr)}{mm} \right]$$

$$mmrm = \frac{2P_{m/r}P^2_{r/m}(1-P_{m/r})}{D} \quad \left[= \frac{2(mmr)(mrm)}{mr} \right]$$

$$mmrr = \frac{2P_{m/r}P_{r/m}(1-P_{m/r})(1-P_{r/m})}{D} \quad \left[= \frac{(mmr)(mrr)}{mr} \right]$$

$$rmmr = \frac{P^2_{m/r}P_{r/m}(1-P_{m/r})}{D} \quad \left[= \frac{(mmr)^2}{4mm} \right]$$

$$mrmr = \frac{2P^2_{m/r}P^2_{r/m}}{D} \quad \left[= \frac{4(mrm)(rmr)}{mr} \right]$$

$$mrrm = \frac{P_{m/r}P^2_{r/m}(1-P_{r/m})}{D} \quad \left[= \frac{(mrr)^2}{4rr} \right]$$

$$rrmr = \frac{2P^2_{m/r}P_{r/m}(1-P_{r/m})^2}{D} \quad \left[= \frac{2(rrm)(rmr)}{mr} \right]$$

$$rrrm = \frac{2P_{m/r}P_{r/m}(1-P_{r/m})^2}{D} \quad \left[= \frac{(mrr)(rrr)}{rr} \right]$$

$$rrrr = \frac{P_{m/r}(1-P_{r/m})^3}{D} \quad \left[= \frac{(rrr)^2}{rr} \right]$$

$$D = P_{m/r}(1-P_{r/m}) + 2P_{m/r}P_{r/m} + P_{r/m}(1-P_{m/r})$$

The relationships in brackets of the preceding equations hold for Bernoulli as well as for first-order Markov statistics.

The second-order Markov process is characterized by eight conditional probabilities, four of which are independent. In this statistical model, the monomer addition process is influenced not only by the monomer unit on the growing end, but by the one preceding it (the penultimate unit). All of the tactic sequences can be described in terms of the four independent probabilities listed below but due to the rather lengthy mathematical notation necessary for these tactic sequences the reader is referred to page 159 of Reference 17 for the actual relationships. Here,

$$P_{mm/m} = \frac{mmm}{mm} \qquad P_{rm/m} = \frac{mmr}{mr}$$

$$P_{mm/r} = \frac{mmr}{2(mm)} \qquad P_{rm/r} = \frac{2(rmr)}{mr}$$

$$P_{mr/m} = \frac{2(mrm)}{mr} \qquad P_{rr/m} = \frac{mrr}{2(rr)}$$

$$P_{mr/r} = \frac{mrr}{mr} \qquad P_{rr/r} = \frac{rrr}{rr}$$

the first two subscripts refer to the configuration of the last two monomer units on the growing chain end and the last subscript represents the placement of the incoming monomer unit.

The final statistical model that will be mentioned here was advanced by Coleman and Fox[18-20] mainly to describe the block-like configurations exhibited by many homogeneous anionic polymerizations. In this mechanistic scheme the tacticity at the end of the propagation center

exerts no influence on the mode of addition of the next monomer unit. Coleman and Fox proposed that blocky configurations were propagated because the growing chain end existed in (a minimum of) two states which might correspond to chelation by the counterion or chelation by solvation. The duration of the chelation by the solvating species would then determine the length of each block. In each state, the propagation statistics were assumed to be Bernoullian, although the probability of either an m or r placement was presumed to be different for each state. This type of statistical model generates chain sequences which cannot be described by Bernoullian or any finite order Markovian statistic. Further details as well as the mathematical expressions for all the tactic sequences, are given on pages 160-166 of Reference 17 and References 18-22.

From pentad tacticity the Bernoulli, first-order Markov and second order Markov models can be tested. This means that a polymer can be shown to be either consistent or inconsistent with the given model at that level of sequence discrimination. The second order Markov model cannot be tested with only tetrad information even though it is possible to test both the first-order Markov and Bernoulli models. Only triad data is required to test the Bernoulli model but it is not sufficient to check either Markov model. In fitting the appropriate model it is sufficient only to show that four of the six tetrad relationships and six of the ten pentad relationships are satisfied[17].

Considering the first-order Markov model, there are four possible types of chains which can be generated from the two probabilities, $P_{m/r}$ and $P_{r/m}$ and are as follows[17]:

1.	Block	$P_{m/r}<0.5$ $P_{r/m}<0.5$	$\Sigma P<1$
2.	Heterotactic-Like ("Alternating")	$P_{m/r}>0.5$ $P_{r/m}>0.5$	$\Sigma P>1$
3.	Isotactic-Like	$P_{m/r}<0.5$ $P_{r/m}>0.5$	$\Sigma P = 1$ for Bernoullian Statistics
4.	Syndiotactic-Like	$P_{m/r}>0.5$ $P_{r/m}<0.5$	

Polymers of types 3 and 4 can be generated by Bernoullian propagation where the limits are the pure stereochemical polymer forms. For a pure heterotactic polymer $P_{m/r} = P_{r/m} = 1.0$. Tables 4-25, 4-26, and 4-27 show the values of these two probabilities for the isotactic, atactic and syndiotactic polymers, respectively. In addition, these tables give the specific persistence ratio which expresses the tendency of the r and m units to propagate themselves preferentially and is defined as[18,19]:

$$\rho = \frac{2(m)(r)}{mr}$$

In the case of $\rho > 1$, the lengths of the m or r sequences will be longer than those produced by Bernoulli statistics having the same composition of m units. On the other hand, a value of $\rho < 1$ indicates that the lengths of the m or r sequences will be shorter than for Bernoulli statistics. Thus, a value of $\rho > 1$ is a measure of the stereoblock

Table 4-25. Configurational Statistics of the Isotactic Poly(alkyl α-bromoacrylate)s[a,b]

Ester	m	r	$P_{m/r}$	$P_{r/m}$	ρ	ΣP	Z	Polymer Type
Methyl	0.81	0.19	0.16	0.68	1.18	0.84	2.40	Isotactic-like
Ethyl	0.79	0.21	0.17	0.66	1.23	0.83	2.53	Isotactic-like
n-Propyl	0.84	0.16	0.12	0.63	1.34	0.75	2.45	Isotactic-like
i-Propyl	0.75	0.25	0.20	0.60	1.25	0.80	2.67	Isotactic-like
n-Butyl	0.79	0.21	0.18	0.67	1.14	0.85	2.13	Isotactic-like
n-Pentyl	0.83	0.17	0.15	0.71	1.13	0.86	2.24	Isotactic-like

a. synthesized with the modified Grignard complex
b. from carbonyl carbon resonance

Table 4-26. Configurational Statistics of the Atactic Poly(alkyl α-bromoacrylate)s[a,b]

Ester	m	r	$P_{m/r}$	$P_{r/m}$	ρ	ΣP	Z	Polymer Type
Methyl	0.32	0.68	0.69	0.33	0.99	1.02	0.95	Syndiotactic-like
Ethyl	0.34	0.66	0.68	0.35	0.98	1.03	0.89	Syndiotactic-like
n-Propyl	0.33	0.67	0.72	0.34	0.94	1.06	0.73	Syndiotactic-like
i-Propyl	0.33	0.67	0.66	0.32	1.02	0.98	1.07	Syndiotactic-like
n-Butyl	0.32	0.68	0.72	0.33	0.95	1.05	0.77	Syndiotactic-like
n-Pentyl	0.32	0.68	0.69	0.33	0.99	1.02	0.95	Syndiotactic-like

a. synthesized with Decanoyl Peroxide at 50°C
b. from carbonyl carbon resonance

Table 4-27. Configurational Statistics of the Syndiotactic Poly(alkyl α-bromoacrylate)s[a,b]

Ester	m	r	$P_{m/r}$	$P_{r/m}$	ρ	ΣP	Z	Polymer Type
Methyl	0.18	0.82	0.84	0.19	0.95	1.03	0.82	Syndiotactic-like
Ethyl	0.20	0.80	0.85	0.21	0.94	1.06	0.74	Syndiotactic-like
n-Propyl	0.21	0.79	0.81	0.22	0.98	1.03	0.86	Syndiotactic-like
i-Propyl	0.22	0.78	0.78	0.23	0.98	1.01	0.98	Syndiotactic-like
n-Butyl	0.21	0.79	0.81	0.22	0.95	1.03	0.80	Syndiotactic-like
n-Pentyl	0.19	0.81	0.85	0.20	0.94	1.05	0.71	Syndiotactic-like

a. synthesized with Benzoin at -40°C
b. from carbonyl carbon resonance

character in a polymer and a value of $\rho < 1$ indicates an alternating character in the polymer.

An additional criterion for Bernoullian statistics is that the

$$z = \frac{4(mm)rr}{(mr)^2}$$

quantity Z should be either close or equal to unity. Although this is an extremely sensitive test, its value should be unity for a Bernoullian chain[20].

All of the samples in Table 4-25 were polymerized anionically by the complexed Grignard initiator and displayed all of the features expected for an isotactic-like polymer. For instance, the $P_{m/r}$ value was considerably less than 0.5 which indicated that the probability was low for locating an r unit after an m unit, and furthermore, the high $P_{r/m}$ value signified that the probability was very high for encountering an m unit after an r unit. Thus, these two probabilities illustrated the preference of the propagating chain to add monomer units by solely isotactic placement.

The value of the specific persistence ratio, ρ, being slightly greater than one demonstrated the tendency for the m units to exist in a blocky manner. The fact that ρ exceeded one only slightly indicated that the r units were placed in a random manner. The slight deviation of ρ from unity and the rather large deviation in excess of unity for z revealed that the isotactic polymers did not conform to Bernoullian statistics.

Somewhat surprising was that none of these isotactic polymers had the stereoblock character which was found for a series of

poly(alkyl α-chloroacrylate)s synthesized with the same initiating system[9]. It was possible that the low syndiotactic block content resulted because of the presence of only one active catalyst complex. This catalyst complex which would be formed from equal amounts of the two co-catalysts, methyl magnesium chloride and benzalacetophenone, should not produce any significant blockiness of r units. Although slight imperfections or momentary solvent changes in the catalyst complex could be responsible for the addition of some r units, the large scale propagation of r groups into blocks should be absent. The fact that the poly(alkyl α-chloroacrylate)s could be fractionated into two portions, one being predominately isotactic and the other predominately atactic, was evidence for the presence of two different propagating mechanisms. The absence of a blocky nature in the poly(alkyl α-bromoacrylate)s was a fairly good indication for the purity of the catalyst complex used in the polymerizations.

The data in Table 4-26 for the atactic polymers and in Table 4-27 for the syndiotactic polymers demonstrated conclusively that both of these polymer types followed Bernoullian statistics. In all cases the specific persistence ratio, ρ, and ΣP were very close to unity with the deviations never in excess of 6%. Both the atactic and syndiotactic polymers were synthesized with free radical initiators and therefore were expected to obey Bernoullian statistics[9,17]. The atactic samples were polymerized with decanoyl peroxide at 50°C while the syndiotactic samples were prepared at -40°C employing ultraviolet light and benzoin as the photo-initiator.

The effect of the polymerization temperature on the relative production of m and r units was reflected very well by the two polymerization probabilities, $P_{m/r}$ and $P_{r/m}$. For example, the atactic polymers had $P_{m/r}$ values between 0.66 and 0.72 as compared to 0.78 to 0.85 for the syndiotactic polymers. The higher values for the latter series indicated a higher tendency for an r unit to follow an m unit as should be the case for a syndiotactic-rich polymer. Similarly, the syndiotactic samples had lower $P_{r/m}$ values than the isotactic samples, again reflecting the predominance of the r units.

The Bernoullian behavior of the atactic and syndiotactic polymers was further demonstrated by the values of the quantity z which were relatively close to unity. The slight deviation from one for this quantity was probably due in part to the sensitive nature of the test[17], in particular to its dependence on the value of mr. Nevertheless, the relative closeness of z to unity for these two polymer types still indicated that they followed Bernoullian statistics. It should be noted that although the term atactic polymer has been used for the samples in Table 4-26, they were still predominately syndiotactic polymers.

The experimental propagation statistics of all the isotactic poly(alkyl α-bromoacrylate)s were generated fairly well by a first-order Markov process as shown in Table 4-28. All of these samples were synthesized with the modified Grignard complex using methyl magnesium chloride and benzalacetophenone in a one-to-one molar ratio, as described in Chapters II and III.

According to Bovey[17], the criteria for applicability of first-order Markovian statistics is that four of the six tetrad values calculated

Table 4-28. Calculated First-Order Markov Tetrads versus Experimental Tetrads for Isotactic Poly(alkyl α-bromoacrylate).

Ester	Tetrads[a]					
	rrr	rmr	rrm	mmr	mrm	mmm
Ethyl	0.04	0.04	0.06	0.17	0.09	0.60
	0.03	0.03	0.07	0.22	0.10	0.55
n-Propyl	0.02	0.02	0.05	0.15	0.06	0.70
	0.02	0.02	0.06	0.18	0.07	0.65
i-Propyl	0.03	0.03	0.10	0.20	0.10	0.54
	0.03	0.03	0.11	0.24	0.09	0.50
n-Butyl	0.02	0.03	0.08	0.19	0.09	0.59
	0.02	0.03	0.09	0.23	0.10	0.53
n-Pentyl	0.01	0.02	0.07	0.17	0.08	0.65
	0.01	0.02	0.07	0.21	0.09	0.60

a. first line is experimental tetrad values; second line is first-order Markov tetrad values.

from the $P_{m/r}$ and $P_{r/m}$ probabilities must agree within experimental error with experimentally determined tetrads. For the five esters presented in Table 4-28, the experimental rrr, rmr, rrm and mrm tetrads agreed very well with those generated by the non-random first-order Markov process. The values for the remaining two tetrads, mmr and mmm, were not as close as the other four but were still reasonably close, usually within 5%. As a matter of fact, the sum of the mmr and mmm experimental values were very close to the sum of the mmr and mmm calculated values. Considering the experimental error resulting from the lack of detail in some of the ^{13}C NMR spectra, an error of 5% was reasonable. Furthermore, the specific persistence ratio, ρ, (Table 4-25) was equivalent to $1/\Sigma P$ which is an additional requirement for Markovian statistics.

Table 4-29 displays the pentad propagation statistics for all of the isotactic polymers except the i-propyl ester where pentad assignments were not possible. In the case of pentad tacticity the criteria for applicability of first-order Markovian statistics was that six of the ten experimentally determined pentad values must agree within experimental error to the pentad values calculated from the $P_{m/r}$ and $P_{r/m}$ probabilities[17]. In general, the agreement between the experimental and calculated pentad values for rrrr, rrrm, rrmr, mrmr, mrrm, mmrr and mmrm were excellent for all of the esters. The closeness of the mmmr and mmmm values were reasonably good with only the mmmr pentad displaying rather poor agreement. Perhaps in this case the poor agreement was a consequence of the poor separation observed for this peak in most of the spectra. In any event, it was apparent that the propagation statistics of these polymers were duplicated fairly well by

Table 4-29. Calculated First-Order Markov Pentads versus Experimental Pentads for Isotactic Poly(alkyl α-bromoacrylate).

Ester	Pentads[a]									
	rrrr	rrrm	rrmr	mrmr	mrrm	mmrr	rmmr	mmmm	mmrm	mmmm
Methyl	0.01	0.02	0.02	0.03	0.05	0.03	0.05	0.09	0.14	0.56
	0.01	0.02	0.01	0.03	0.03	0.03	0.06	0.17	0.13	0.51
Ethyl	0.01	0.02	0.02	0.03	0.04	0.08	0.09	0.08	0.12	0.51
	0.01	0.02	0.02	0.03	0.03	0.08	0.03	0.19	0.14	0.45
n-Propyl	0.01	0.01	0.02	0.03	0.03	0.04	0.05	0.07	0.11	0.63
	0.01	0.02	0.01	0.02	0.02	0.07	0.04	0.13	0.11	0.57
n-Butyl	0.01	0.02	0.02	0.04	0.04	0.07	0.08	0.07	0.16	0.49
	0.01	0.02	0.01	0.03	0.02	0.07	0.04	0.16	0.13	0.51
n-Pentyl	--	0.02	0.02	0.03	0.05	0.07	0.06	0.08	0.12	0.55
	0.01	0.02	0.01	0.02	0.03	0.06	0.04	0.17	0.13	0.51

a. first line is experimental tetrad values; second line is first-order Markov tetrad values.

a non-random first-order Markov process. A similar statistical tetrad analysis by Dever and co-workers[9] also demonstrated that a series of poly(alkyl α-chloroacrylate)s synthesized with the modified Grignard complex obeyed first order Markovian statistics.

Although the second-order Markovian propagation statistics were not presented, their agreement was found to be poorer than for the first-order Markovian propagation statistics for both the tetrad and pentad values.

Figure 4-19 displays the full scale isotactic, atactic and syndiotactic ^{13}C NMR spectra for the methyl ester, poly(methyl α-bromoacrylate). The similar spectra for the ethyl, n-propyl, i-propyl, n-butyl and n-pentyl esters are exhibited in Figures 4-20 through 4-24, respectively.

Summary and Conclusions

The 19 mHz ^{13}C NMR spectra have been obtained for isotactic, atactic and syndiotactic samples of six poly(alkyl α-bromoacrylate)s and included the methyl, ethyl, n-propyl, i-propyl, n-butyl and n-pentyl esters. Complete assignments for the ten pentad peaks of the carbonyl carbon resonance were achieved for all but the i-propyl ester while a complete analysis of tetrad tacticity from the backbone methylene carbon resonance was possible for all but the methyl ester. The tetrad values calculated from the experimentally determined pentad contents were found to agree well with the experimental tetrad values. As a result of insufficient peak separation of the quaternary carbon resonance, complete pentad assignments were possible in only a few instances.

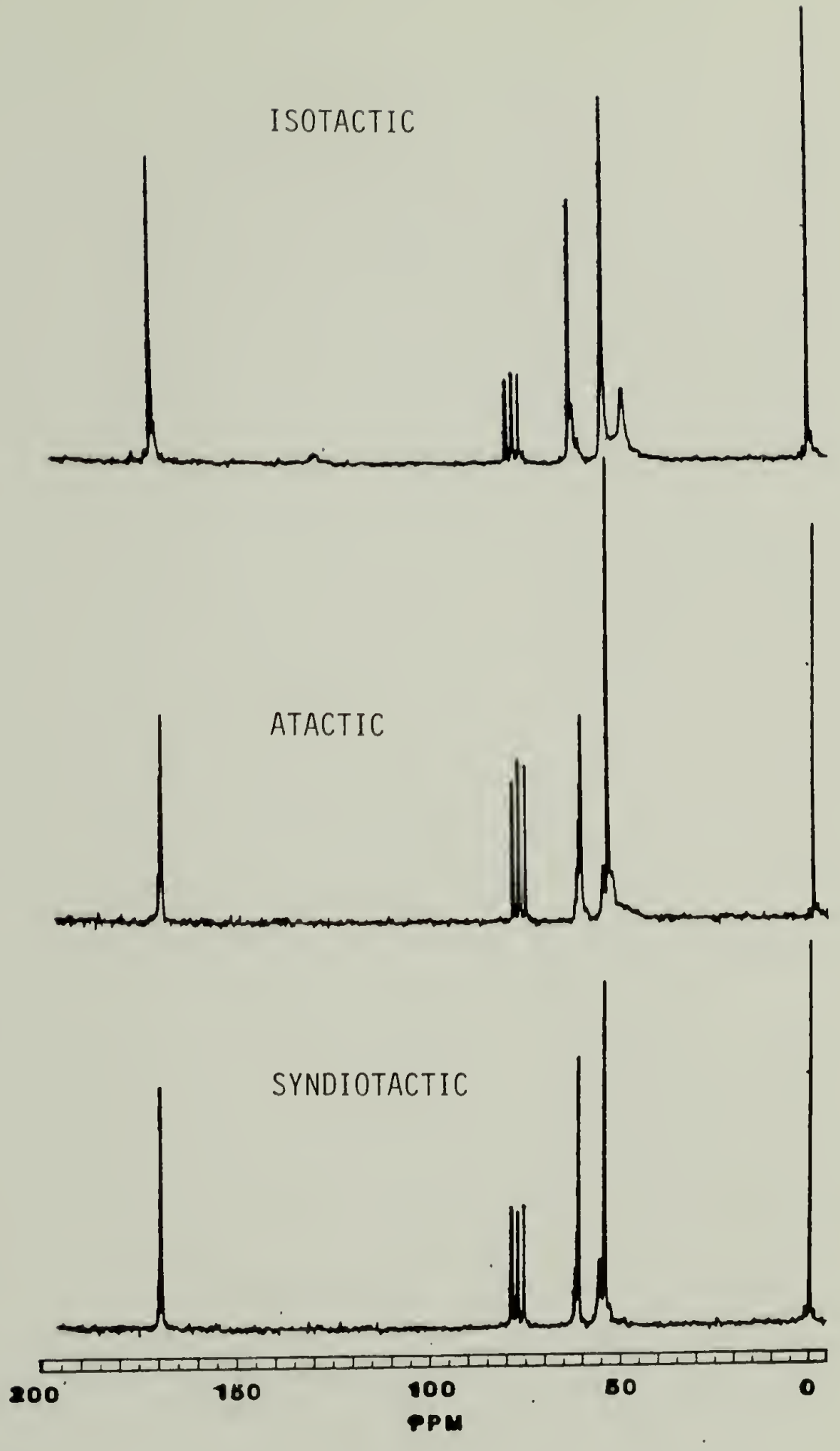


Figure 4-19. The Complete ^{13}C NMR Spectra for Isotactic, Atactic and Syndiotactic Poly(methyl α-bromoacrylate) in ppm Relative to TMS

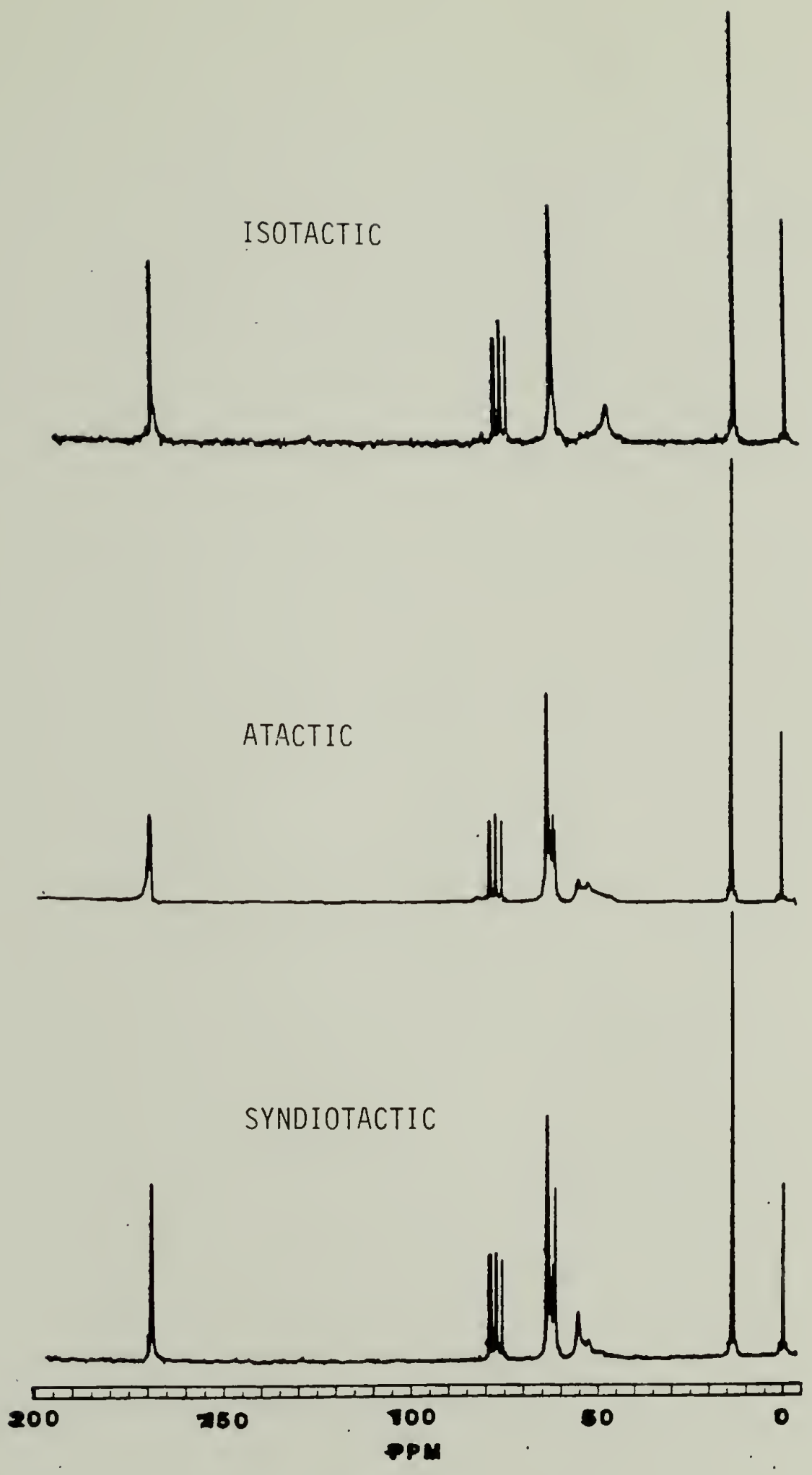


Figure 4-20. The Complete ^{13}C NMR Spectra for Isotactic, Atactic and Syndiotactic Poly(ethyl α-bromoacrylate) in ppm Relative to TMS

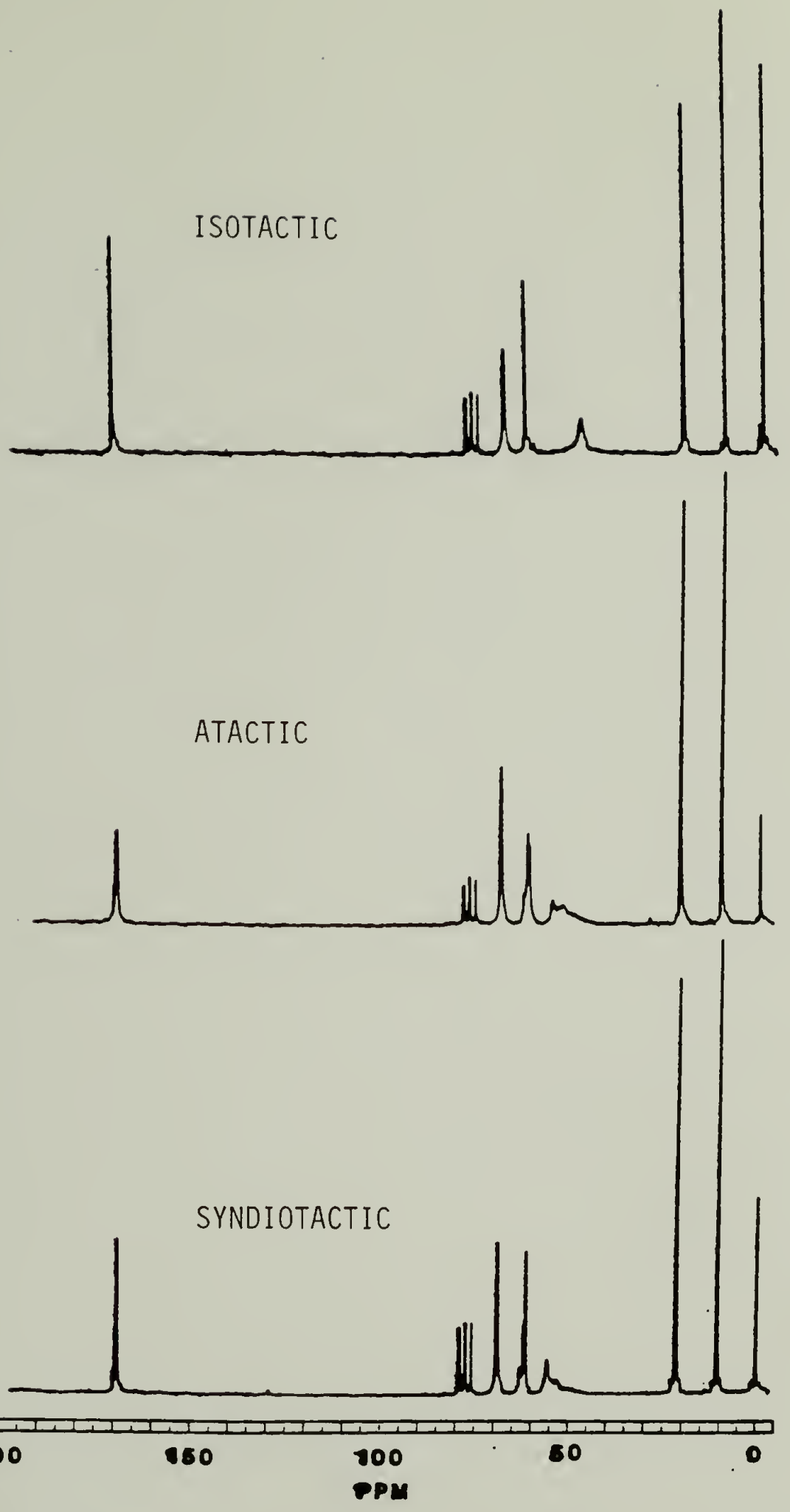


Figure 4-21. The Complete ^{13}C NMR Spectra for Isotactic, Atactic and Syndiotactic Poly(n-propyl α-bromoacrylate) in ppm Relative to TMS

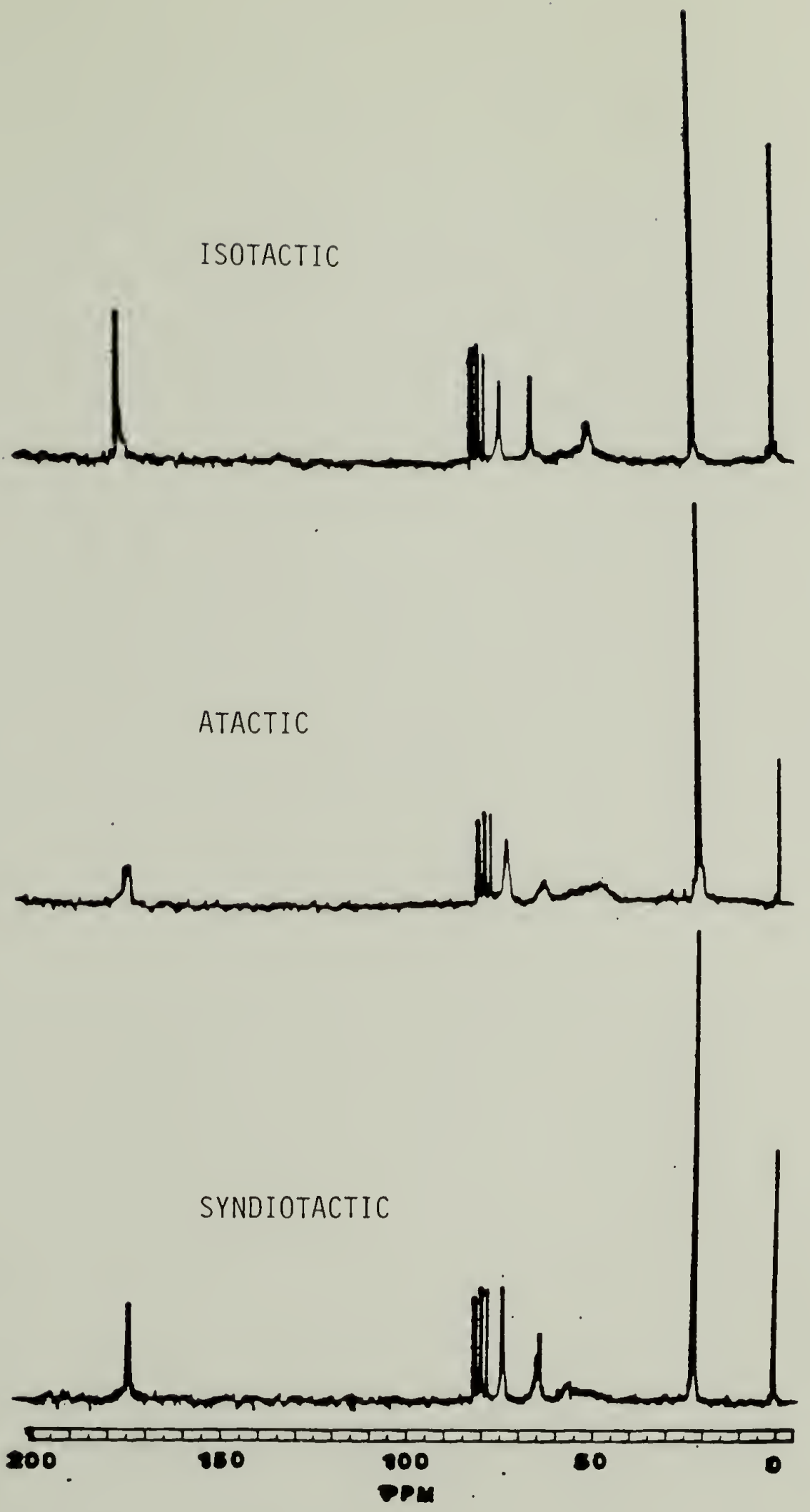


Figure 4-22. The Complete ^{13}C NMR Spectra for Isotactic, Atactic and Syndiotactic Poly(i-propyl α-bromoacrylate) in ppm Relative to TMS

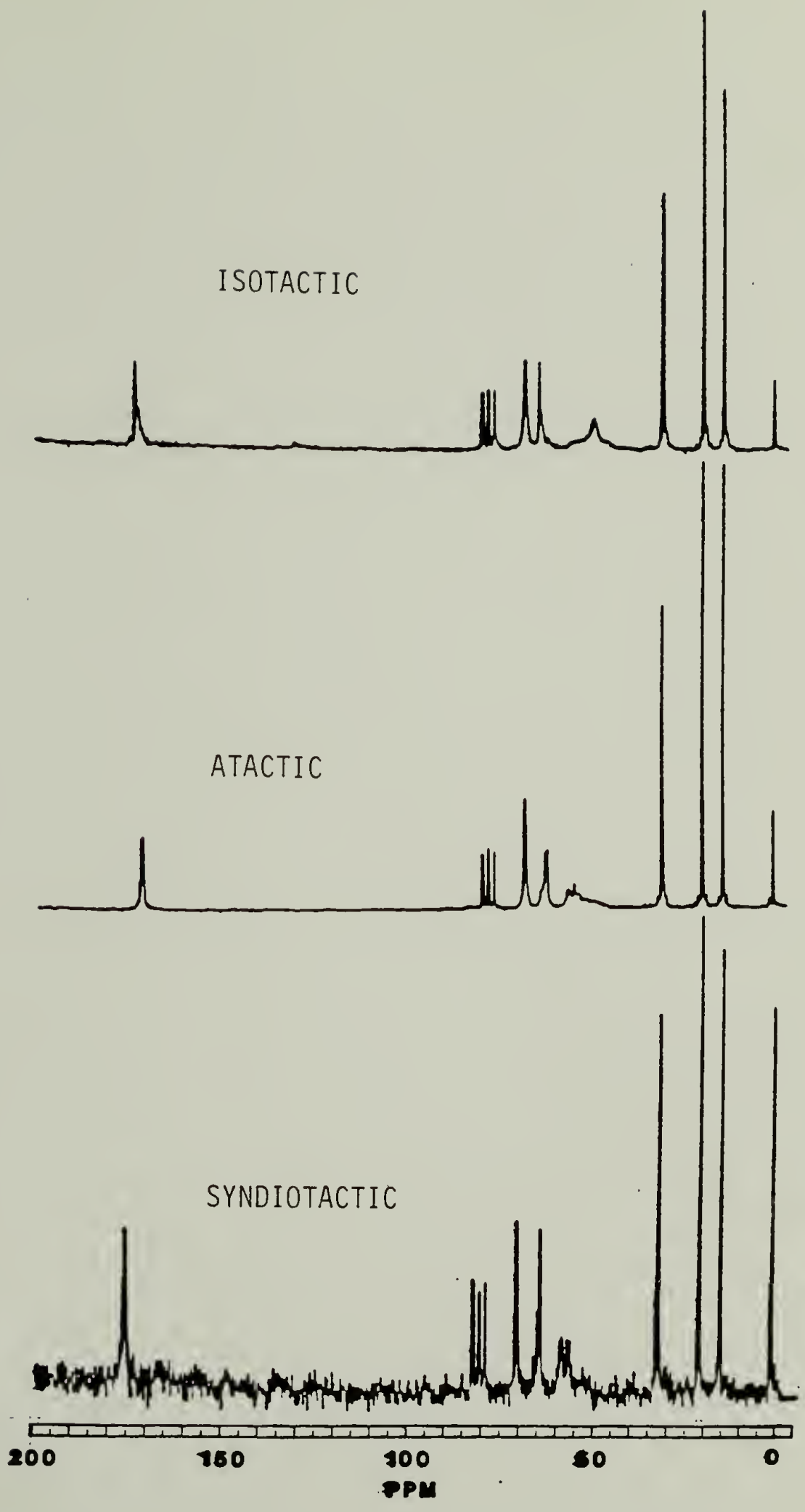


Figure 4-23. The Complete ^{13}C NMR Spectra for Isotactic, Atactic and Syndiotactic Poly(n-butyl α-bromoacrylate) in ppm Relative to TMS

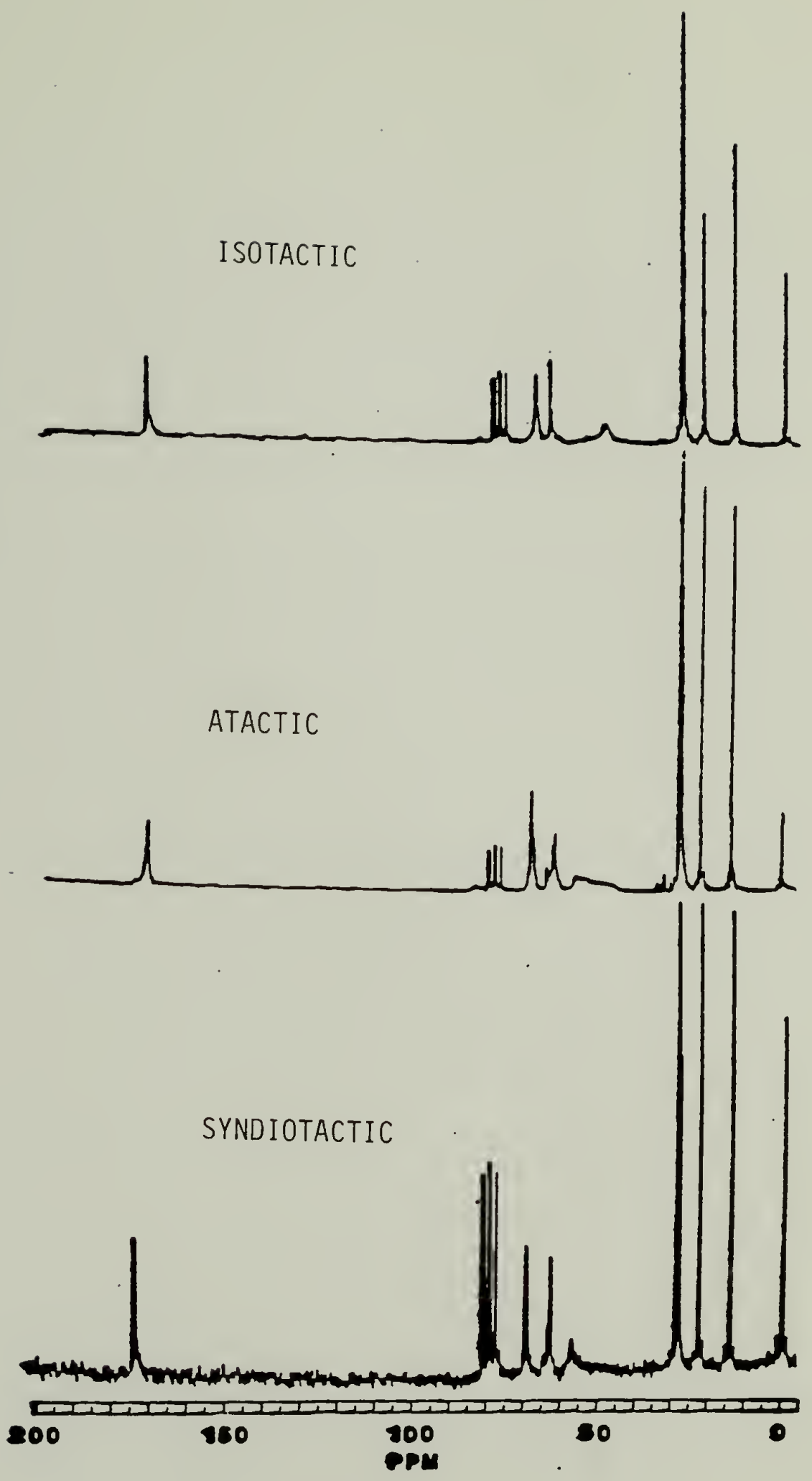


Figure 4-24. The Complete ^{13}C NMR Spectra for Isotactic, Atactic and Syndiotactic Poly(n-pentyl α-bromoacrylate) in ppm Relative to TMS

However, triad tacticity measured from the quaternary carbon resonance was in agreement with triads calculated from both the experimental pentad and tetrad contents.

All of the isotactic samples were found to obey first-order Markovian propagation statistics from an analysis of the m and r sequence distribution. This type of propagation model suggested an influence of the chain end monomer unit upon the steric placement of the incoming monomer molecule, no doubt, as a result of the catalyst structure (modified Grignard complex). For these polymers, the percentage of isotactic units ranged from 60 for the i-propyl ester to 74% for the n-propyl ester, on a triad basis.

Both the atactic and syndiotactic polymers that were synthesized by free radical techniques displayed near perfect Bernoullian statistics. A Bernoullian propagation model indicated that the placement of the incoming monomer unit was independent of the monomer unit on the growing chain end. In other words, the relative amount of r or m placement was dependent solely on the activation energies associated with each tactic form. This phenomenon is typical of polymers synthesized by free radical initiators. The atactic samples were analyzed to be moderately syndiotactic with the rr triads values ranging from 43 to 46%. The syndiotactic samples were prepared at a much lower temperature, -40 versus 50°C and therefore the content of rr groups increased to within the range of 60 and 66%.

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CHAPTER V

LACTONIZATION OF POLY(ALKYL α-BROMOACRYLATE)S

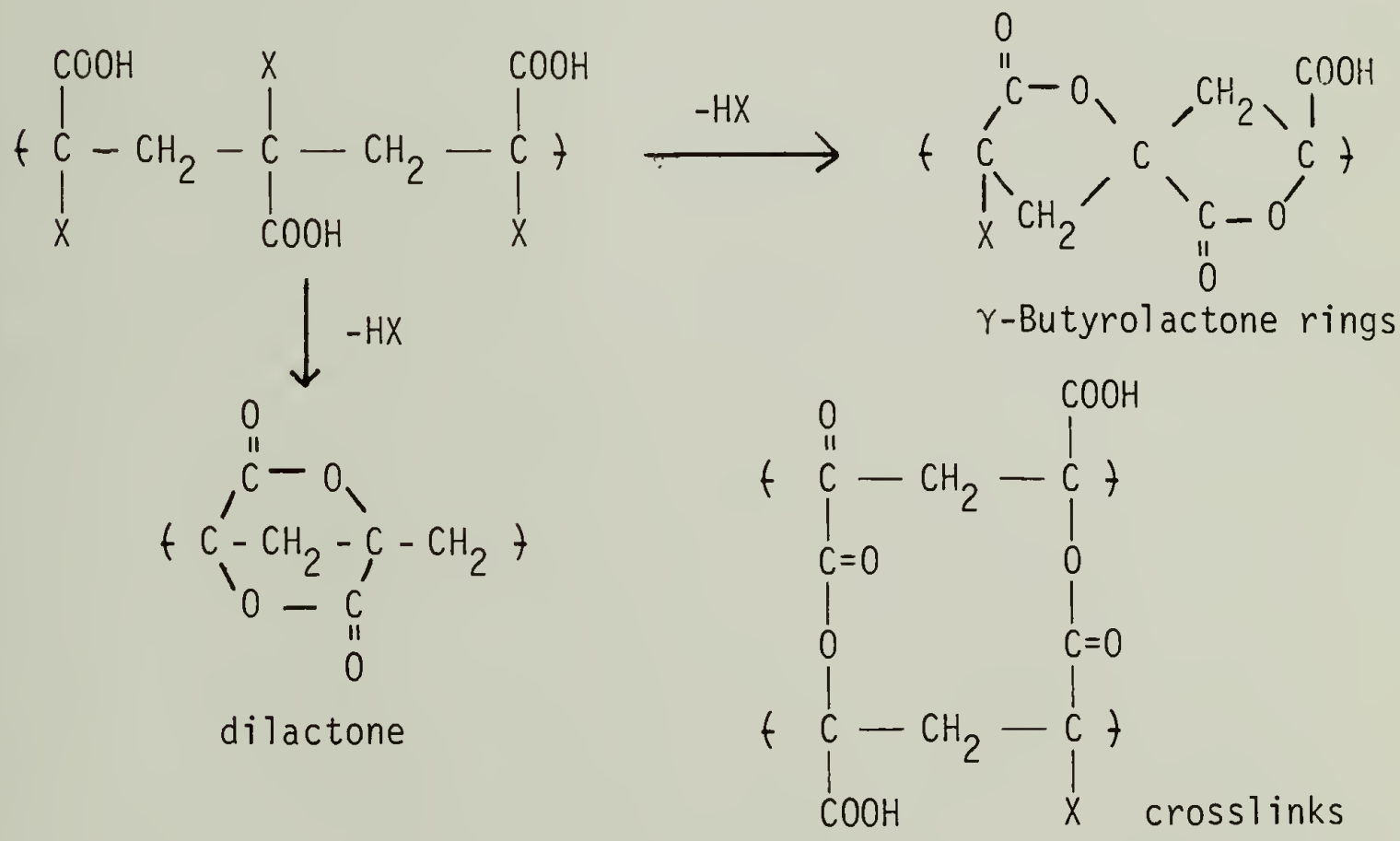
Introduction

The formation of polymers containing lactone rings as part of the backbone was first observed by McNally and VanDyke[1,2] in alternating copolymers of maleic anhydride and vinyl acetate. Upon treatment with alcohol under acidic conditions, the copolymers were found to undergo deacetylation, esterification and lactonization. Lactone formation was also observed when certain copolymers of vinyl acetate and methyl acrylate were hydrolyzed under acid conditions in alcohol solution[3,4].

Marvel and co-workers reported that when a solution of either poly(methyl α-chloroacrylate) or poly(methyl α-bromoacrylate) was refluxed in dioxane containing concentrated sulfuric acid, gel formation occurred and upon drying gave a halogen-free, water insoluble product[5]. The authors indicated that the product was a crosslinked lactone containing both ester and hydroxyl groups and due to the insolubility of the product, a considerable amount of intermolecular crosslinking seemed probable. The possibility for a small degree of lactone formation during the polymerization of the α-chloro and α-bromo esters was mentioned to explain the halogen deficiency in the polymers, although studies of these polymers under neutral conditions were not carried out. Quantitative information was not provided but it was stated that poly(methyl α-chloroacrylate) required a substantially longer treatment than the corresponding α-bromoacrylate polymer before the onset of

lactonization. The appearance of a carbonyl absorption band at 1794 cm^{-1} was attributed to the lactone carbonyl peak and was taken as evidence for the formation of lactone rings.

An investigation by Watanabe and Murano[6] revealed similar evidence for lactone formation for the polymers of the α-chloro and α-bromo-acrylic acids. When the polyacids were heated in the solid state, the elimination of the appropriate hydrogen halide was observed with the apparent formation of butyrolactone rings.



It was assumed that the corresponding intermolecular crosslinking reaction did not occur at early stages of the reaction and that the dilactone structure could not form due to the restrictions on the bond angles of carbon and oxygen. Quantitative measurements of the lactone contents were determined from the 1725 cm^{-1} absorption band of the polymer carbonyl and the γ-butyrolactone carbonyl absorption at 1795 cm^{-1}.

The rate of lactonization of poly(α-chloroacrylic acid) was several times lower than poly(α-bromoacrylic acid) where, even at room temperature, hydrogen bromide was eliminated. Lactonization studies were only conducted with isotactic and syndiotactic samples of poly(α-chloroacrylic acid).

The isotactic polymer was polymerized in the solid state (35°C) and was thought to be predominately isotactic but did not appear to be highly stereoregular based on the NMR spectrum. The same polymerization conducted in the liquid state at 85°C was said to have mainly the syndiotactic configuration but was probably much closer to an atactic polymer. Higher rates of lactone formation were found for the isotactic polymers as compared to the syndiotactic polymers. The difference in the lactone yields between the two polymers was attributed to the difference in the polymer microstructure rather than differences in molecular weight, even though a dependence of intrinsic viscosity on the degree of lactonization was found. For instance, after 10 minutes at 156°C, degrees of lactone formation of 20 and 30% were observed between two isotactic polymers having intrinsic viscosities of 2.2 and 1.0. In most cases this difference was larger than the differences in lactone formation measured between the isotactic and syndiotactic polymers. The intrinsic viscosities of the isotactic and syndiotactic polymers were stated to be 1.2 and 2.5 respectively, so it is difficult to determine the exact effect of the tacticity on the degree of lactone formation.

The authors expected that poly(α-chloroacrylic acid) would exist in a 5_2 helix, being analogous to poly(methyl methacrylate). The

isotactic configuration would then facilitate the elimination of hydrogen chloride and hence, lactone formation. Considering the planar zig-zag structure, lactone formation would be favored by the syndiotactic configuration.

The preparation of γ-butyrolactone rings along the backbone of poly(ethyl α-chloroacrylate) was achieved by Smets and Flore[7] using a Friedel-Crafts catalyst, aluminum trichloride. Presumably, the mechanism involved an intramolecular nucleophilic substitution reaction with internal cyclization. The measurement of the chlorine loss in the polymers indicated that degrees of lactone formation approaching 60% could be achieved. In addition, the number average molecular weight fell to almost 75% of the initial value which was slightly more than expected and indicative of some polymer degradation. All of the polymers employed in this investigation were atactic as they were polymerized with a free radical initiator at 85°C.

Experimental

Lactonization. The lactone containing polymers were prepared from both solid state and solution reactions at temperatures ranging from 70 to 150°C. Initially the reactions were carried out under both nitrogen and air atmospheres but the results were identical in both cases, so atmospheric conditions were employed in the majority of the studies. All of the solution studies were conducted in 1,1,2,2-tetrachloroethane because of its high boiling point, 146°C, and its ability to function as a suitable solvent for the isotactic polymers (only chloroform was better). Concentrations of 2.5% (w/v) were

employed for the solution reactions for two reasons. First, it was difficult to prepare some of the isotactic polymers, such as the i-propyl, n-butyl and n-pentyl esters in higher concentrations without heating and secondly, at concentrations less than 2.5% difficulty was encountered in precipitating the syndiotactic polymers from solution.

The syndiotactic polylactones displayed a very high solubility (25%) in solvents such as 1,1,2,2-tetrachloroethane and chloroform while the isotactic polymers showed only a slight increase in solubility. The polylactones were precipitated by the addition of 10 mls of methanol, filtered and dried in a vacuum at ambient temperature. These samples, as well as the ones prepared in the solid state, were then dissolved in spectral grade chloroform and reprecipitated into methanol. After a minimum of four precipitations, the polymers were dried as before for 24 to 36 hours. When prepared below 100°C, the polylactones were white powdery solids but above this temperature they exhibited a yellowish tint which was not removed even after six purifications. This was probably a result of conjugation (unsaturation) along the polymer backbone.

Elemental analysis. The analytical analysis for bromine content in the polymers was carried out by the Microanalytical Laboratory of the University of Massachusetts.

Infrared spectroscopy. The infrared analysis of the polylactones were measured from films cast on sodium chloride plates from 2% w/v solutions in spectral grade chloroform using a Perkin-Elmer model 283 infrared spectrometer. Quantitative analysis of the lactone content was

determined in the absorption mode from the absorption near 1730 cm^{-1} arising from the ester group in the polymer and the absorption at 1800 cm^{-1} attributed to the ester group of the γ-butyrolactone unit.

Gel permeation chromatography. The molecular weights and molecular weight distributions were measured in tetrahydrofuran solutions using a Waters model 501 gel permeation chromatograph. Concentrations of 0.1 to 0.3% w/v were employed in all cases and the molecular weight calibration curve was determined with narrow molecular weight polystyrene standards under identical conditions.

Nuclear magnetic resonance. All spectra were recorded on a Perkin-Elmer R 32 90 mHz nuclear magnetic resonance spectrometer at temperatures from 80 to 120°C in 5-10% solutions in 1,1,2,2-tetrachloroethane. Tetramethylsiloxane or hexamethyldisoloxane were used as internal standards in all cases.

Evidence for Lactone Formation

Nuclear magnetic resonance. During the initial 90 mHz NMR investigations of atactic poly(ethyl α-bromoacrylate) at 90°C, several peaks uncharacteristic of the polymer appeared. These highly resolved peaks emerged as a triplet and quartet centered at 1.67 and 3.44 ppm relative to tetramethylsilane. Their sharpness indicated a non-polymeric compound (Figure 5-1). The peaks were not observed until the second spectral scan, approximately ten minutes after the sample was heated, and therefore must have resulted from a post-polymerization reaction.

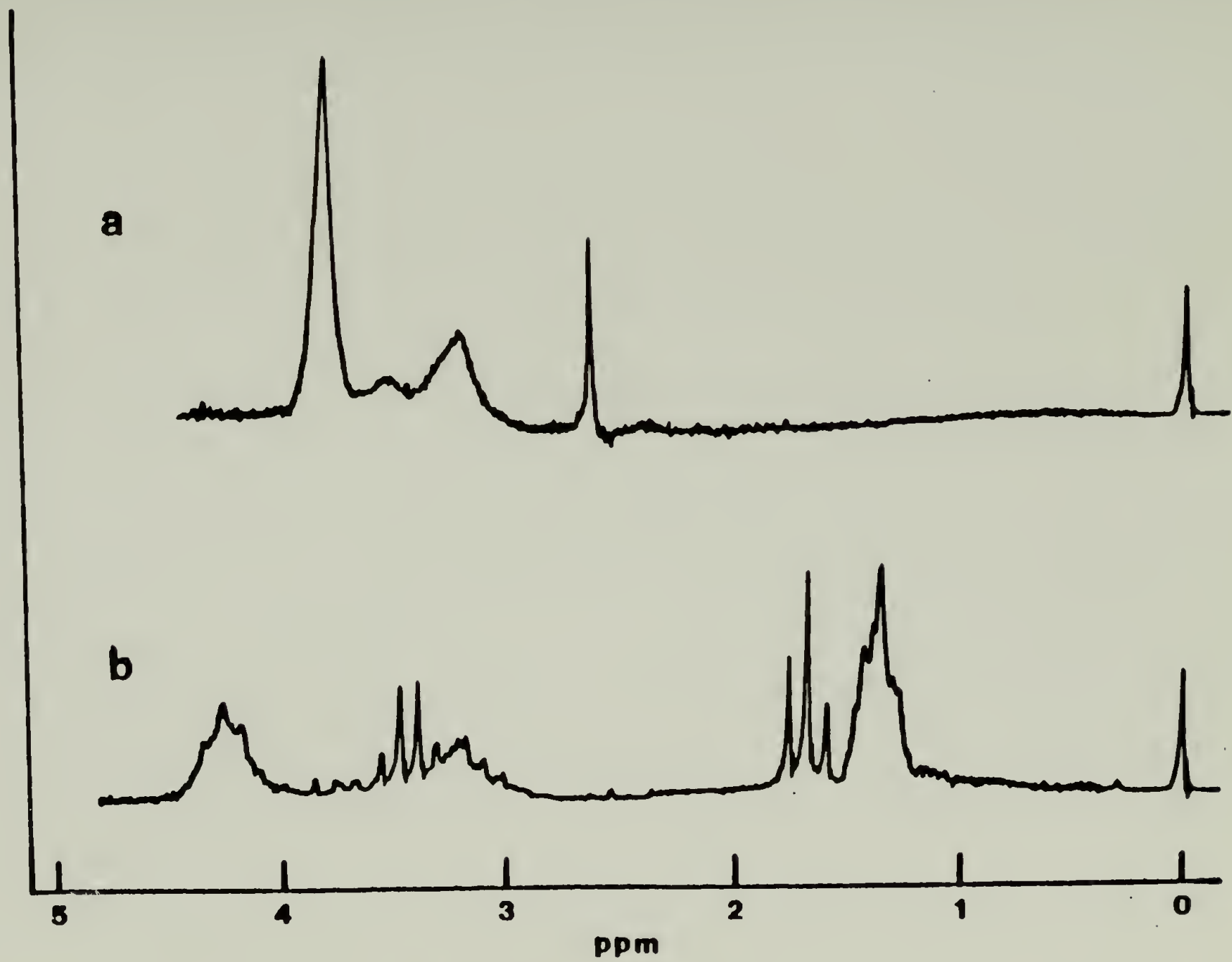


Figure 5-1. Proton NMR Spectra of (a) Poly(methyl α-bromo-acrylate), Sample 4, and Poly(ethyl α-bromo-acrylate), Sample 16, After 30 Minutes at 80°C in 1,1,2,2-Tetrachloroethane

The chemical shifts of the two multiplets were found to correspond exactly to those of ethyl bromide.

Subsequently, poly(methyl α-bromoacrylate) and poly(i-propyl α-bromoacrylate) were found to produce methyl bromide and i-propyl bromide, respectively. Methyl bromide appeared as a singlet at 2.2 ppm (Figure 5-1) and i-propyl bromide displayed a doublet at 1.5 ppm and a quartet at 4.05 ppm as shown in Figure 5-2. As a result of excessive peak overlap, it was not possible to completely identify the alkyl bromides for n-propyl, n-butyl and n-pentyl esters. Quantitative determination of the lactone content was not possible with ^{1}H NMR spectroscopy, again because of peak overlap.

Infrared spectroscopy. All of the polymers in this investigation developed a strong absorption in the vicinity of 1798 cm^{-1}, attributable to the carbonyl of the γ-butyrolactone ring (Figure 5-3). An absorption in this region was characteristic of five-membered lactones and was in agreement with the investigations previously discussed[3,5-7]. The percentage of lactone groups was determined from the area of both the ester absorption at 1730 cm^{-1} and the lactone absorption at 1798 cm^{-1} in a similar manner to Watanabe and Murano[6]. The ratio of extinction coefficients for the two carbonyl peaks appeared to be unity based upon the results obtained from bromine analysis. It was assumed that all of the repeat units contained either ester or lactone groups. In addition, a broad absorption band in the 1200 cm^{-1} region was observed, again characteristic to five-membered lactone rings.

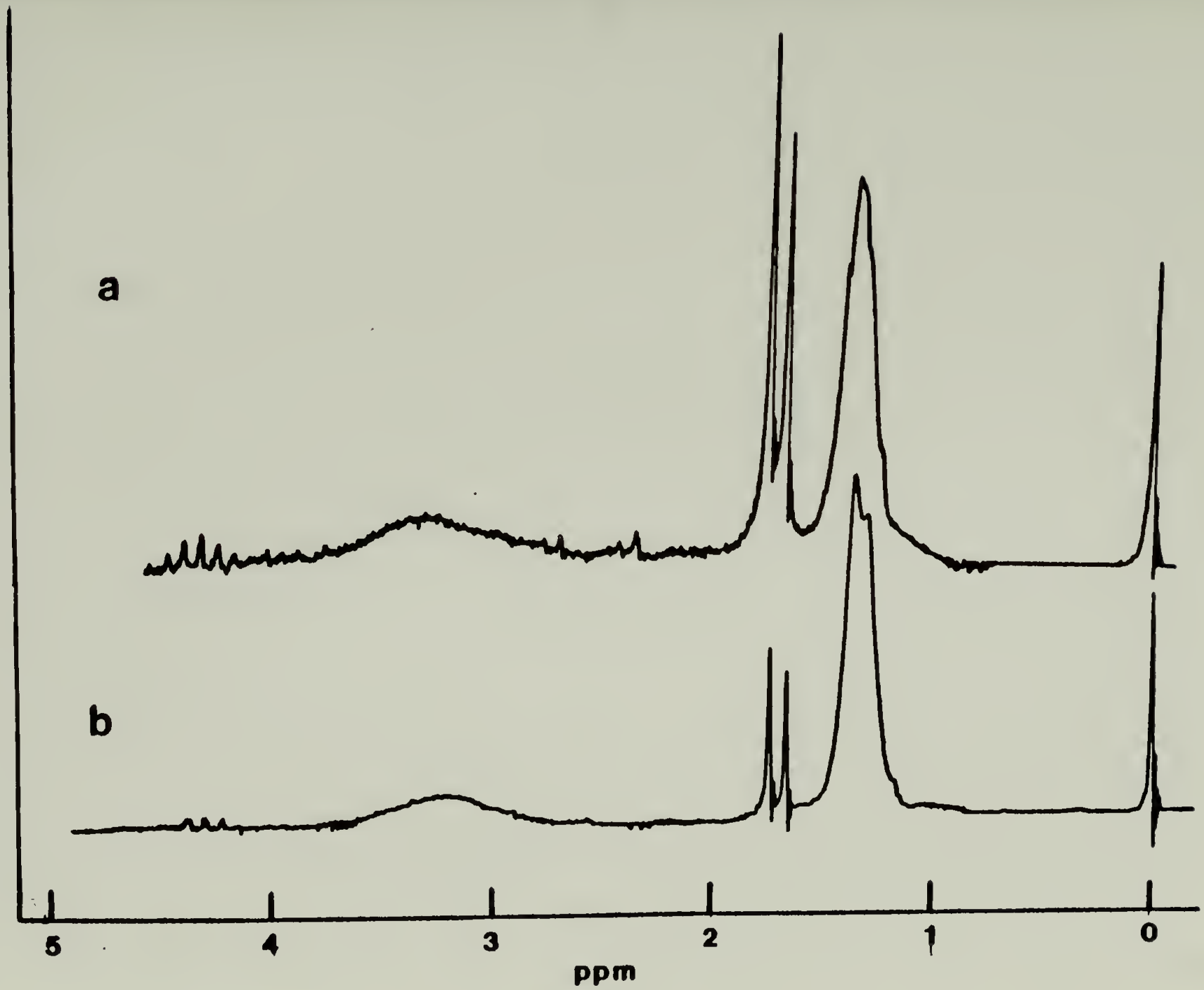


Figure 5-2. Proton NMR Spectra of (a) Poly(i-propyl α-bromo-acrylate), Sample 34, After 30 Minutes and (b) After 15 Minutes at 80°C in 1,1,2,2-Tetrachloro-ethane

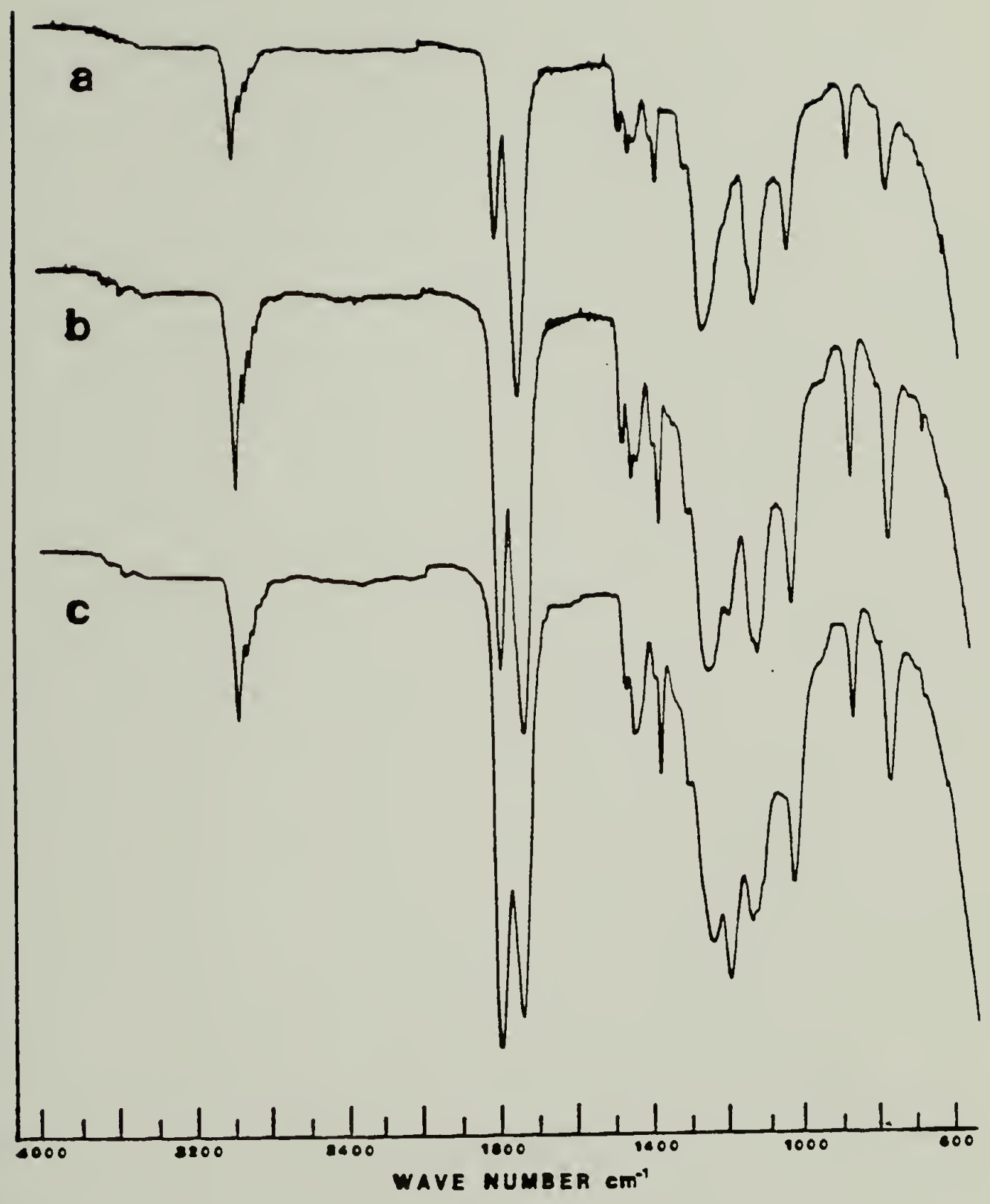


Figure 5-3. Infrared Spectra of Poly(ethyl α-bromoacrylate), Sample 16, (a) After 30 Minutes, (b) After 1 Hour and (c) After 4 Hours at 80°C in 1,1,2,2-Tetrachloroethane

Pyrolysis gas chromatography. Conclusive evidence for the elimination of n-propyl bromide from poly(n-propyl α-bromoacrylate) during heating was furnished by pyrolysis gas chromatography. The retention time of the main component in the polymer chromatogram was matched exactly to that of pure n-propyl bromide. Chromatogram (b) in Figure 5-4 was developed by heating 1 mg of poly(n-propyl α-bromoacrylate) for 15 minutes at 80°C and collecting the products in a liquid nitrogen trap. The trapped compounds were then automatically injected into a chromatograph containing a Poropak Q column. The main component eluting at 16 minutes was expected to be that of the lactonization product n-propyl bromide and the following test proved this to be true. An identical polymer sample was heated as before and the components trapped but in addition, 1 microliter of n-propyl bromide was injected and collected in the same trap. All of the trapped compounds were then automatically injected into the gas chromatograph and trace (a) in Figure 5-4 was obtained. Trace (a) was identical with the trace (b) of the pure polymer except for the enormous increase in the main peak. The fact that both n-propyl bromide and the main degradation product of the polymer eluted together indicated convincingly that they were the same compound. A similar result was achieved with ethyl bromide and poly(ethyl α-bromoacrylate). No effort was directed towards identification of the other components in the polymer chromatograms.

Discussion

Molecular weight studies. A previous investigation[6] indicated a slight dependence of molecular weight on the degree of lactone formation for

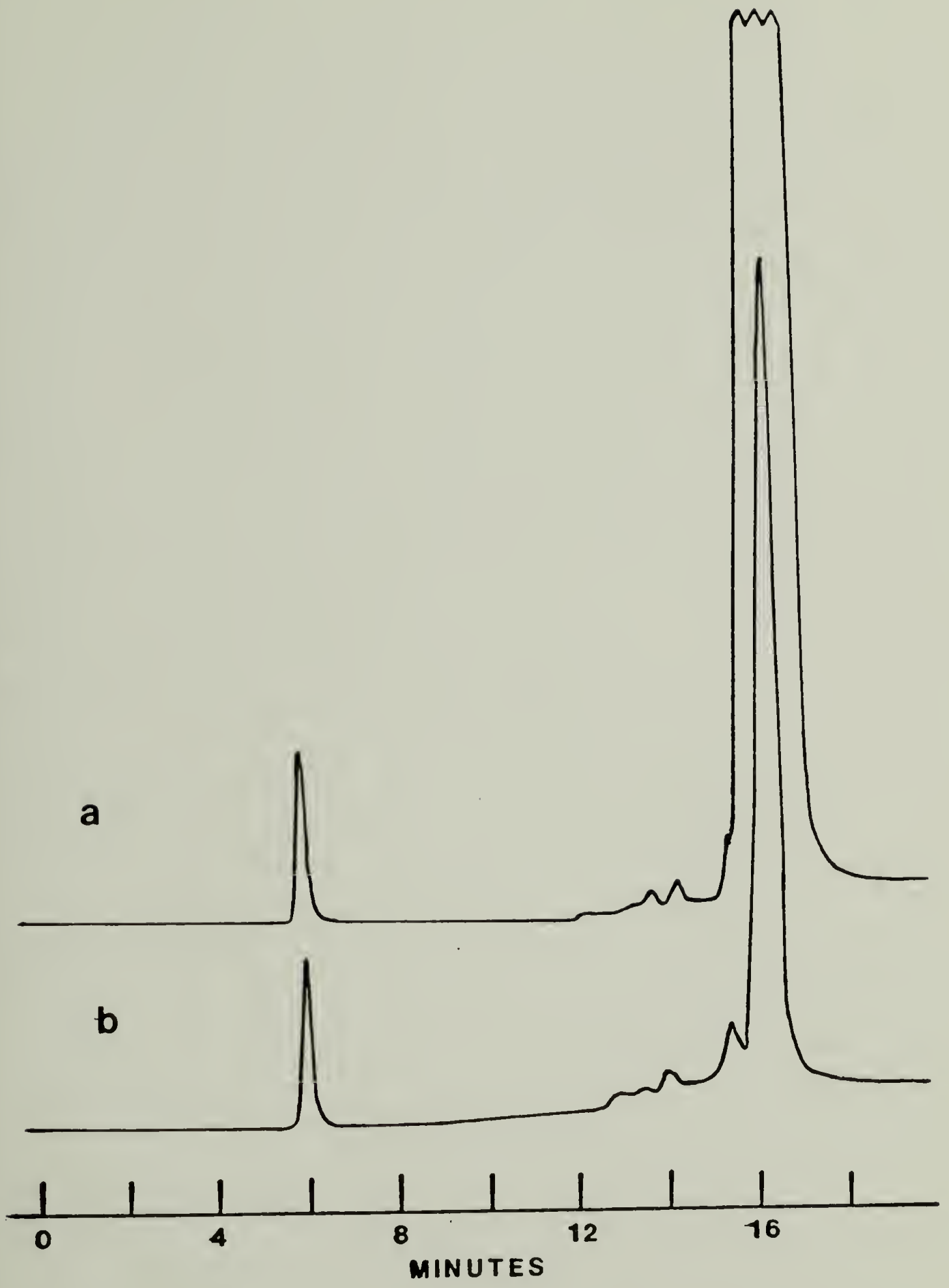


Figure 5-4. Gas Chromatogram of (a) Poly(n-propyl α-bromoacrylate) and n-Propyl Bromide and (b) Only Poly(n-propyl α-bromoacrylate)

poly(α-chloroacrylic acid). The possibility for a similar effect here was shown to be insignificant using two different molecular weight samples of each ester. The molecular weight data reproduced from Table 3-12 is listed in Table 5-1 along with their measured degrees of lactone formation after 4 hours at 80°C. The excellent agreement between the lactonization percentages of each ester indicated an independence of the molecular weight on the overall degree of lactone formation over the molecular weight ranges studied. This result was somewhat expected since essentially all of the polymers were above the low molecular weight range where this type of dependence would be most pronounced. Furthermore, differences in the molecular weight distribution appeared to have little effect on lactonization, as exemplified by samples 24 and 25 where the largest difference in the distributions was found. The dependence observed by Watanabe and Murano[6] may well be due to differences in tacticity for the different molecular weight samples.

Molecular weight and molecular weight distributions were analyzed before and after the lactonization reactions to evaluate the competing effects of the intermolecular and intramolecular reactions. Considering only the occurrence of the intramolecular reaction, the molecular weights should decrease in accordance with the molecular weight loss associated with lactonization. On the other hand, an increase in molecular weight would be reflected by the extent of the corresponding intermolecular reaction. The effect of lactonization on the molecular weights and distributions are shown in Table 5-2 for the isotactic, 5-3 for the syndiotactic and 5-4 for the atactic polymers.

Table 5-1. Effect of Molecular Weight on the Degree of Lactone Formation After 4 Hours at 80°C

Sample	Ester	M_n	M_w	M_w/M_n	% Lactone
4	Methyl	33,000	69,500	2.12	35
5	Methyl	28,000	84,500	3.01	35
16	Ethyl	21,000	53,500	2.58	49
17	Ethyl	40,000	128,500	3.20	49
24	n-Propyl	8,000	27,500	3.44	45
25	n-Propyl	14,500	25,000	1.73	46
32	i-Propyl	26,000	65,000	2.46	54
33	i-Propyl	35,500	109,000	3.07	52
40	n-Butyl	25,500	66,500	2.61	44
41	n-Butyl	20,500	59,500	2.89	44
45	n-Pentyl	33,000	98,500	2.96	48
46	n-Pentyl	44,000	138,000	3.12	47

Table 5-2. Molecular Weights and Molecular Weight Distributions Before and After Lactonization (4 hours at 80°C in 1,1,2,2-Tetrachloroethane).

Isotactic Polymers		Before			After		
Sample	Ester	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n
3	Methyl	31,000	105,000	3.35	35,000	156,000	4.52
14	Ethyl	37,000	114,500	3.09	34,000	148,000	4.41
23	n-Propyl	34,500	108,000	3.12	34,500	180,000	5.26
31	i-Propyl	90,000	291,000	3.24	120,000	601,500	5.03
39	n-Butyl	93,500	280,000	2.99	109,000	538,000	4.97
44	n-Pentyl	89,000	283,000	3.18	92,000	468,000	5.13

Table 5-3. Molecular Weights and Molecular Weight Distributions Before and After Lactonization (4 hours at 80°C in 1,1,2,2-Tetrachloroethane).

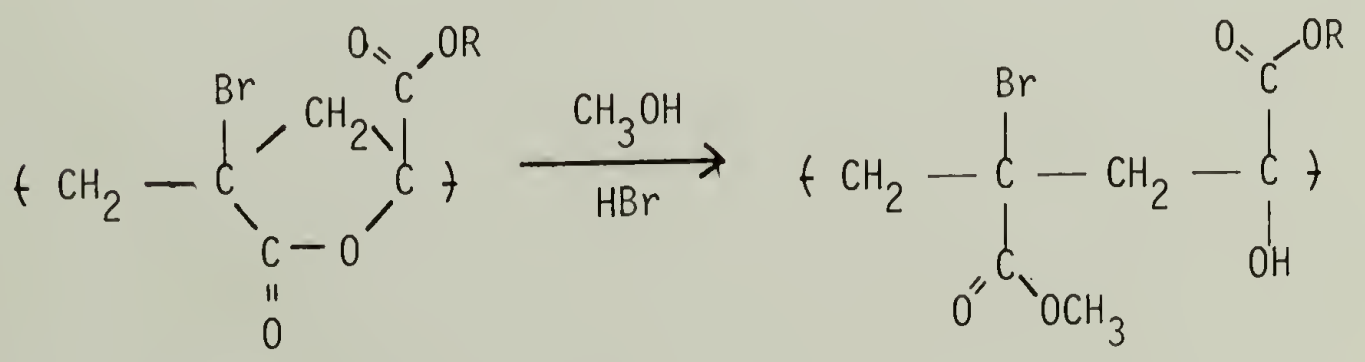
Syndiotactic Polymers		Before			After		
Sample	Ester	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n
8	Methyl	29,500	62,000	2.10	28,000	89,000	3.17
22	Ethyl	42,000	92,000	2.17	39,500	173,000	4.41
30	n-Propyl	44,000	104,500	2.38	43,000	150,000	3.56
36	i-Propyl	45,000	75,000	1.63	35,000	140,000	4.01
43	n-Butyl	48,000	89,000	1.84	42,000	165,000	3.94
47	n-Pentyl	63,000	128,000	2.04	59,000	236,500	4.06

Table 5-4. Molecular Weights and Molecular Weight Distributions Before and After Lactonization (after 4 hours at 80°C in 1,1,2,2-Tetrachloroethane).

Atactic Polymers		Before			After		
Sample	Ester	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n
4	Methyl	33,000	69,500	2.12	30,000	120,000	4.02
16	Ethyl	21,000	53,500	2.58	17,000	73,000	4.33
24	n-Propyl	8,000	27,500	3.44	12,000	53,000	4.49
32	i-Propyl	26,000	65,000	2.46	53,500	225,000	4.27
40	n-Butyl	25,500	66,500	2.61	22,000	70,000	3.27
45	n-Pentyl	33,000	98,500	2.96	29,000	142,000	4.95

Elemental analysis. Excellent agreement was obtained between the degrees of lactone formation determined by infrared and elemental analysis at reaction temperatures below 90°C. Above this temperature, bromine was liberated in a manner other than lactone formation as signified by the divergence of the lactone contents measured by the two techniques. The second part of the discussion section will analyze this in much greater detail.

The percentage of lactone repeating units was calculated from the residual bromine content of the polymer following the lactonization reaction. A minimum of four purifications (see Experimental section) were required to remove all of the alkyl bromide from the polymer. The alkyl bromide was also effectively removed by soxhlet extraction with methanol for one week but esterification of the ring was found to occur. This reaction, as shown below, was apparently catalyzed by traces of hydrogen bromide and resulted in the reformation of ester groups in addition to new hydroxyl groups. The absorbance at 3400 cm^{-1} in the infrared spectrum (Figure 5-5) was evidence for the presence of the alcohol. Esterification of similar polylactones under acidic conditions have also resulted in the formation of hydroxy groups[2-4,7].



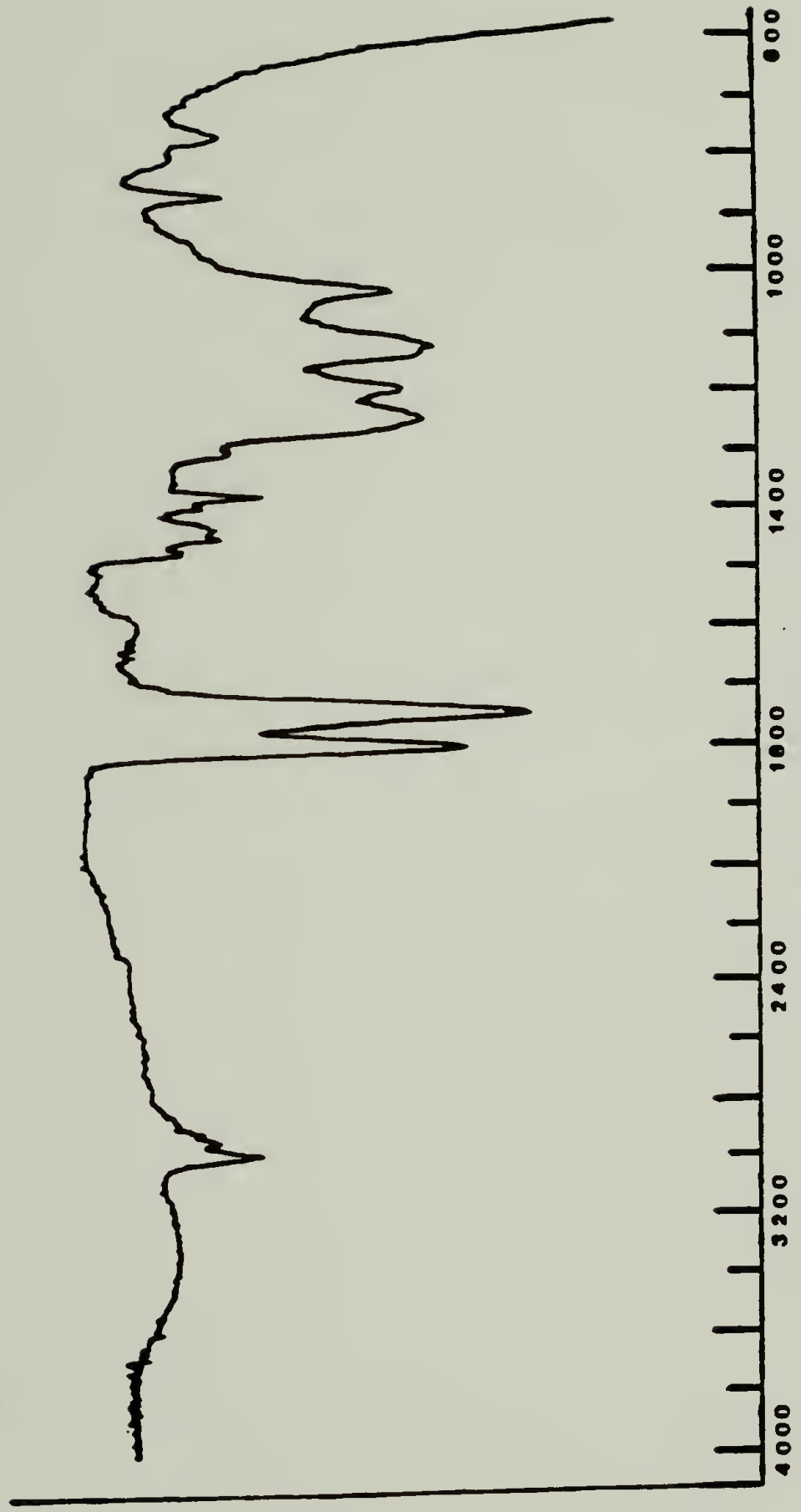


Figure 5-5. Infrared Spectrum of Poly(ethyl α-bromoacrylate), Sample 16, After 1 Hour at 100°C

The decrease in the molecular weight following lactonization occurred for the atactic and syndiotactic samples although the changes were smaller than anticipated. The explanation was undoubtedly due to a small amount of crosslinking resulting from the intermolecular lactone reaction. The loss of the alkyl bromide accompanying lactone formation would account for a molecular weight loss of between 20 and 30% (depending on the size of the ester group) for 50% (1:1 molar ratio) lactone formation. Sample 36, syndiotactic poly(i-propyl α-bromoacrylate) was the only polymer to exhibit the expected 20% decrease in molecular weight. In addition, the weight average molecular weights increased substantially more than the corresponding number average molecular weights as demonstrated by the large increase in the polydispersities.

The number average molecular weights increased for all of the isotactic samples, suggesting a higher degree of crosslinking for these samples. The isotactic configuration inhibited intramolecular lactonization as compared to the syndiotactic configuration and thereby promoted the intermolecular reaction.

Lactonization reactions in the solid state apparently increased the frequency of the intermolecular reaction as illustrated by the increase in both the number and weight average molecular weights. Table 5-5 presents degrees of lactone formation and their corresponding molecular weights for atactic poly(ethyl α-bromoacrylate) from both solid state and solution reactions. The crosslinking reaction became increasingly important for the solid state reaction with conversion as evidenced by the molecular weight increase and partial insolubility of the products.

Table 5-5. Effect of Lactonization on Molecular Weight and Molecular Weight Distribution for Solid State versus Solution Reactions for Atactic Poly(ethyl α-bromoacrylate) at 80°C.

Reaction	Time(min)	M_n	M_w	M_w/M_n	% Lactone
Solid State	15	19,500	62,000	3.2	10
Solid State	60	22,000	86,000	3.9	19
Solid State	180	25,500	130,000	5.1	23
Solution	15	19,000	64,500	3.4	16
Solution	60	19,000	66,500	3.5	27
Solution	180	17,000	70,000	4.1	41

Effect of temperature on lactonization. A considerable difference in the degree of lactone formation calculated from residual bromine content and infrared absorption spectroscopy were observed at reaction temperatures above 80°C. Table 5-6 displays the results from the lactonization of poly(methyl α-bromoacrylate), sample 4, and poly(ethyl α-bromoacrylate), sample 16, from 2.5% solutions in 1,1,2,2-tetrachloroethane at 150°C. The agreement was good for reaction times below 1 hour but at longer times the loss of bromine was considerably greater than the degree of lactonization would justify based on the infrared analysis. One plausible explanation was attributed to dehydrobromination which would produce unsaturation in the polymer backbone. The appearance of an absorption bond at 1600 cm^{-1} in poly(ethyl α-bromoacrylate), Figure 5-4, was evidence for this. Table 5-7 shows lactonization data for poly(ethyl α-bromoacrylate) at 80°C where it was seen that the agreement was still not satisfactory at long reaction times but was improved considerably. After 240 minutes the two methods differed by only 8% at 100°C as compared to 36% at 150°C. The loss of hydrogen bromide was certainly a feasible reaction at the temperatures employed in these investigations. The lactonization data at 80°C in Table 5-8 for isotactic and syndiotactic poly(methyl α-bromoacrylate) show essentially identical results from the two techniques. The agreement was particularly good for the isotactic polymers. Apparently, at this low temperature, side reactions involving the loss of bromine were of only minimal importance. Investigations at temperatures of 70 and 75°C revealed similar agreement but the degrees of lactone formation were

Table 5-6. Determination of Lactone Content from Infrared Analysis and Bromine Content for Atactic Poly(methyl α-bromoacrylate) and Poly(ethyl α-bromoacrylate) After Lactonization at 150°C.

Ester	Time(min)	% Lactone From Br %	% Lactone From IR
Methyl	5	29	28
Methyl	30	46	45
Methyl	60	52	48
Methyl	240	86	50
Ethyl	5	33	31
Ethyl	30	56	51
Ethyl	60	62	54
Ethyl	240	90	54

Table 5-7. Determination of Lactone Content from Infrared Analysis and Bromine Content for Atactic Poly(ethyl α-bromoacrylate) after Lactonization at 100°C.

		% Lactone	
Ester	Time(min)	From Br %	From IR
Ethyl	10	25	26
Ethyl	30	39	37
Ethyl	60	46	45
Ethyl	120	53	49
Ethyl	240	61	53

Table 5-8. Determination of Lactone Content from Infrared Analysis and Bromine Content for Isotactic and Syndiotactic Poly-(methyl α-bromoacrylate) after Lactonization at 80°C

Tactic Form	Time(min)	% Lactone	
		From Br %	From IR
Isotactic	30	10	9
Isotactic	60	13	13
Isotactic	120	18	19
Isotactic	240	25	25
Syndiotactic	30	12	10
Syndiotactic	60	16	15
Syndiotactic	120	24	23
Syndiotactic	240	39	37

significantly lower, especially for the isotactic polymers. In view of this information the remainder of the work was conducted at 80°C.

A study by Watanabe and Murano[6] on poly(α-bromoacrylic acid) revealed degrees of lactone formation of 40% after 10 minutes at 156°C measured by infrared spectroscopy. Unfortunately, the bromine contents of the polylactones were not reported so it is impossible to determine the extent of possible side reactions.

Lactonization in solution versus solid state. Significantly higher rates of lactone formation were achieved for the reactions conducted in solution relative to those in the solid state. Figure 5-6 for atactic poly(ethyl α-bromoacrylate) showed this exceptionally well. The reactions in solution displayed degrees of lactonization of almost 20% higher after 3 hours at 80°C, as well as a considerably faster initial rate. The effect of reaction temperature for the solid state reactions are shown in Figure 5-7. The rates were affected substantially less by temperature than the corresponding solution reactions. Presumably, the increased reactivity resulted from the added chain flexibility (freedom of rotation) imparted to the polymer in solution and allowed the reacting pendent ester groups more freedom to rotate into conformations more amenable for lactonization. The early leveling off displayed by the reactions in the solid state could have been partly due to an increase in the chain stiffness introduced by the rigid lactone structures but it is more likely that the intermolecular cross-linking reaction exhibited the greater effect. The influence of

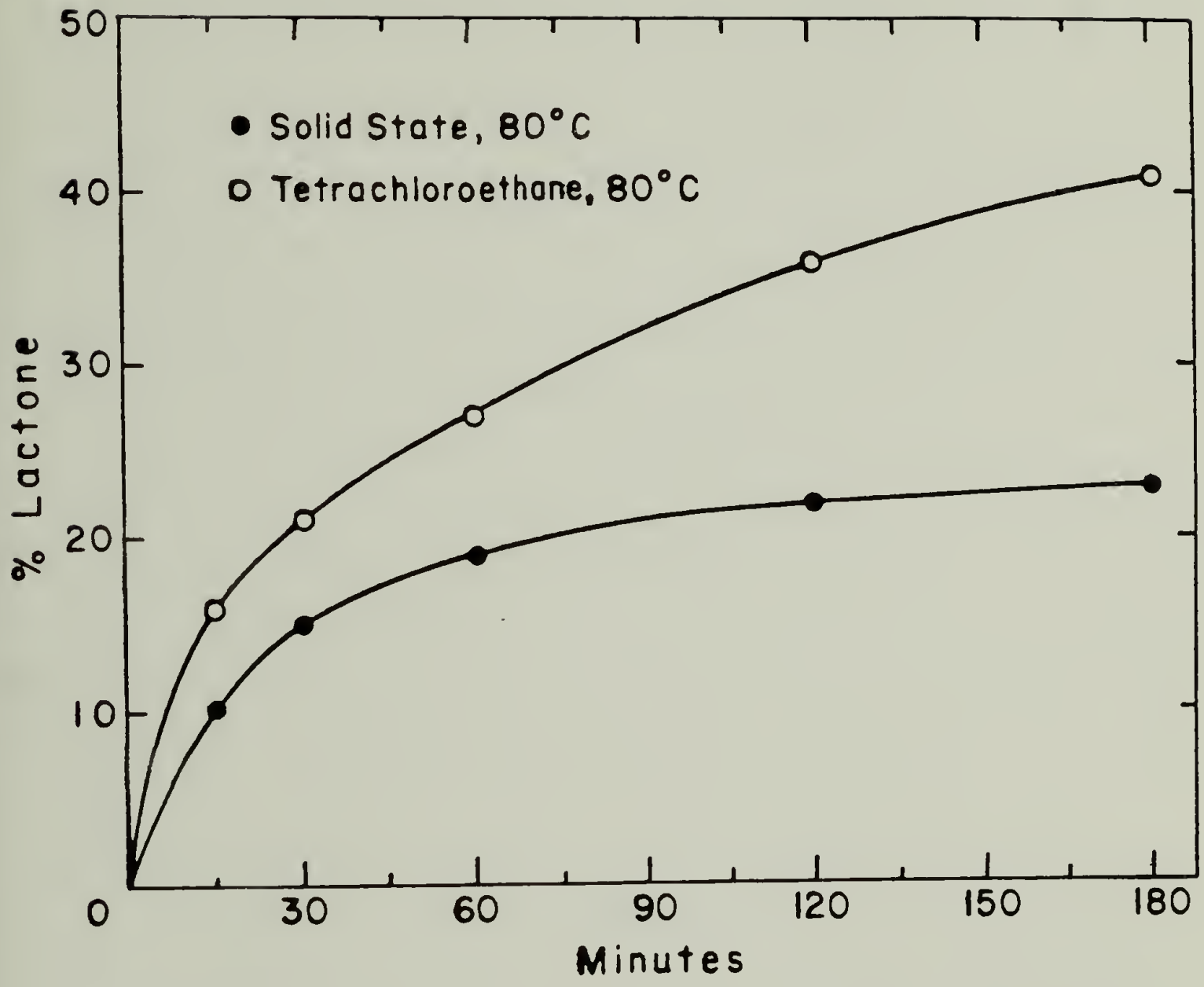


Figure 5-6. Rate of Lactonization for Atactic Poly(ethyl α-bromoacrylate), Sample 16, in Solid State and Solution at 80°C

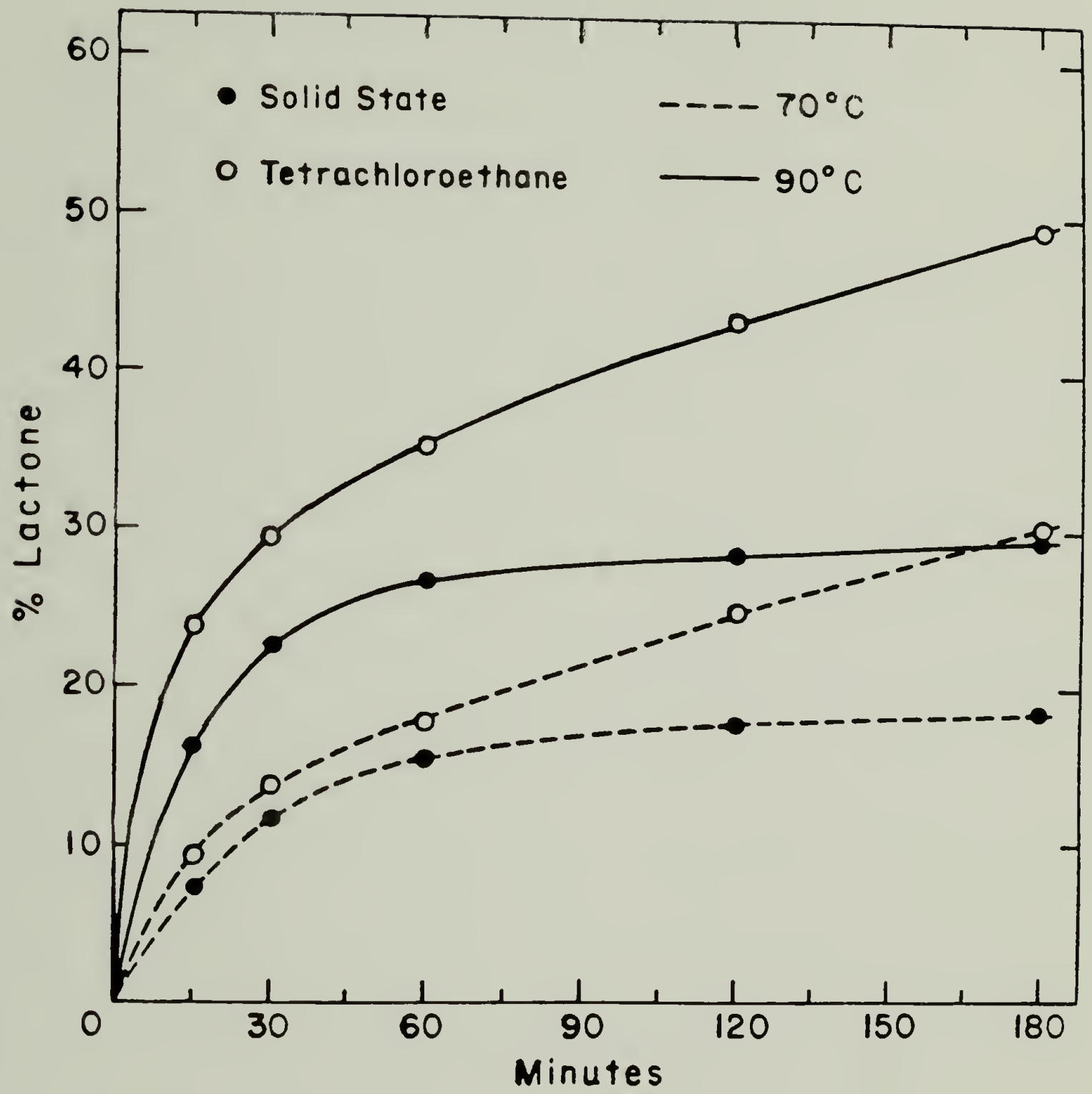


Figure 5-7. Rate of Lactonization for Atactic Poly(ethyl α-bromoacrylate), Sample 16, in Solid State and Solution at 70 and 90°C

polymer tacticity on the degree of lactone formation in the solid state was not investigated.

Effect of tacticity and ester group on lactonization. Figures 5-8 through 5-12 examine the effects of polymer tacticity on the rate of lactone formation for six different alkyl esters. All reactions were conducted in 2.5% w/v solutions in 1,1,2,2-tetrachloroethane at 80°C. All of the syndiotactic polymers displayed a significantly higher reactivity towards lactonization than the corresponding isotactic polymers. Table 5-9 lists the six ester groups in an increasing order of reactivity towards lactone formation where the values corresponded to a four-hour reaction time. The same trend was displayed for both the isotactic and syndiotactic esters. The differences of 12 to 16% in the degree of lactonization for the isotactic and syndiotactic forms were attributed to the polymer configuration. Although the two configurations should have existed in the trans conformation in solution, the spatial relationships of the two reacting groups would have been different for each form. The syndiotactic configuration allowed for relatively close contact between the reacting groups (assuming only intramolecular lactonization) and facilitated lactone formation. The isotactic structure prevented such close contact and therefore hindered lactonization. In the isotactic configuration all of the bromine atoms lie either above or below the molecular plane, making close contact between the bromine and the ester oxygen difficult. On the other hand, the syndiotactic form consists of the bromine atoms and the ester groups

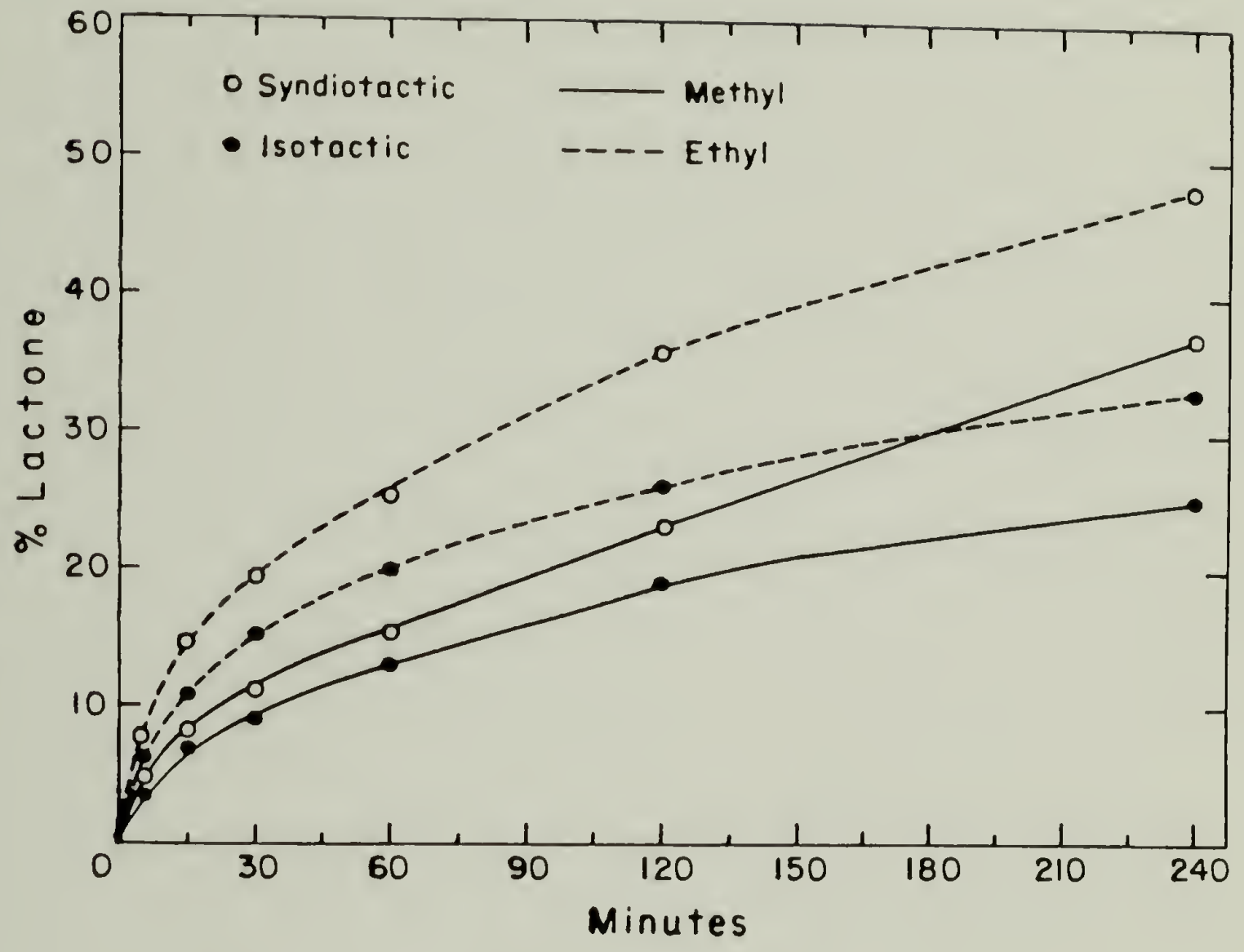


Figure 5-8. Rate of Lactonization for Isotactic and Syndiotactic Poly(methyl α-bromoacrylate) and Poly(ethyl-α-bromoacrylate) in Solution at 80°C

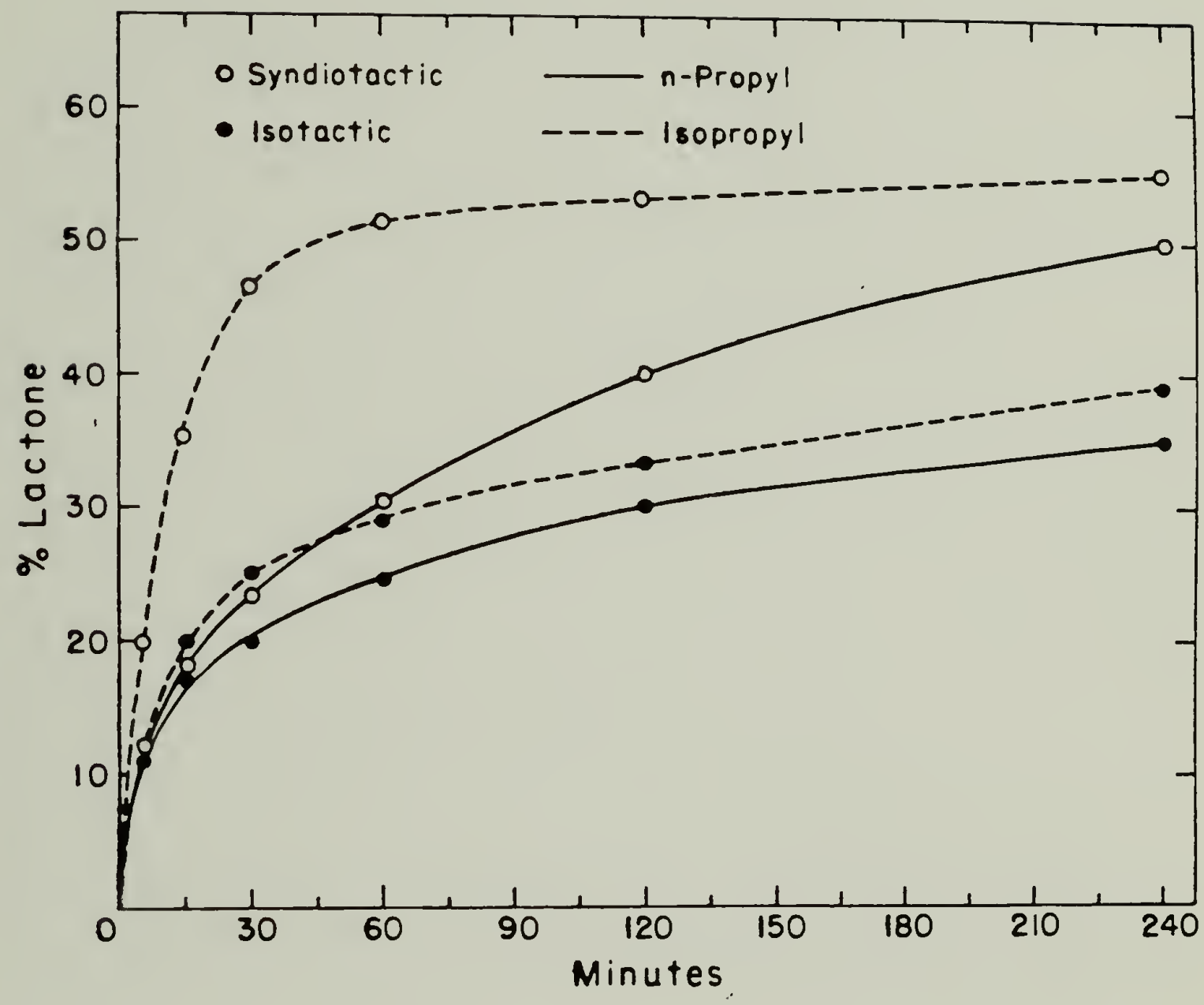


Figure 5-9. Rate of Lactonization for Isotactic and Syndiotactic Poly(n-propyl α-bromoacrylate) and Poly(i-propyl α-bromoacrylate) in Solution at 80°C

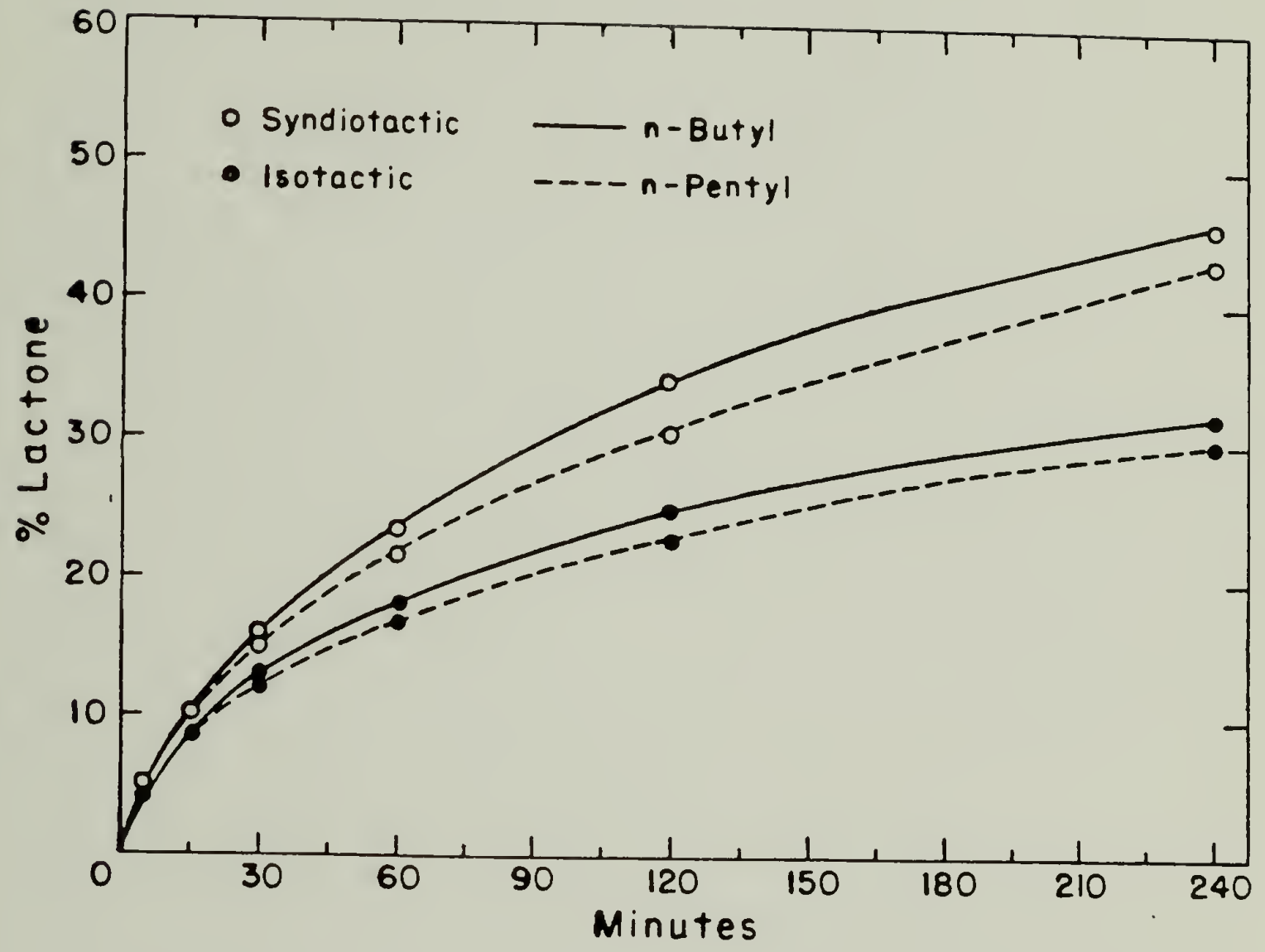


Figure 5-10. Rate of Lactonization for Isotactic and Syndiotactic Poly(n-butyl α-bromoacrylate) and Poly(n-pentyl α-bromoacrylate) in Solution at 80°C

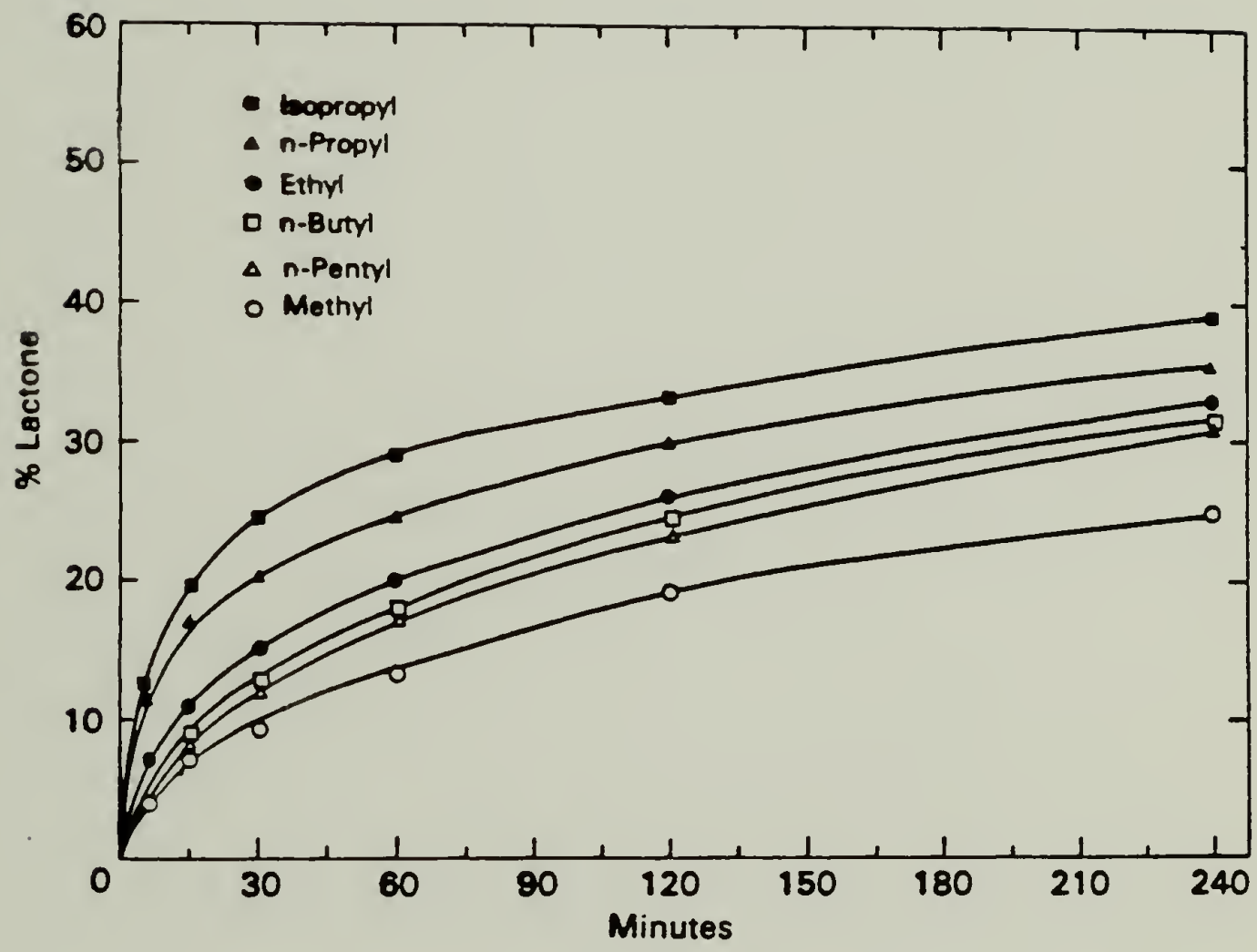


Figure 5-11. Rate of Lactonization for Six Isotactic Poly-(alkyl α-bromoacrylate) Esters in Solution at 80°C

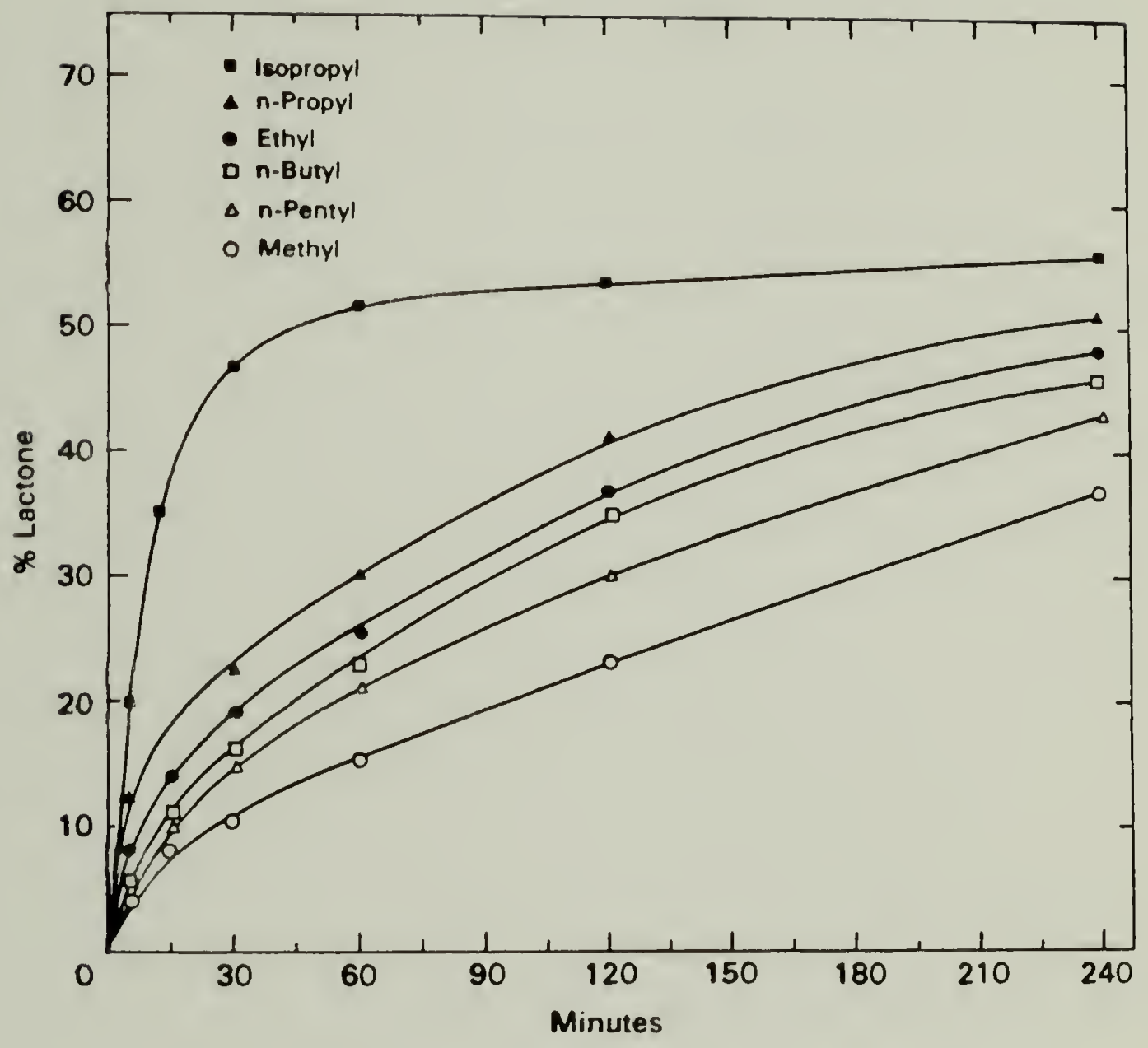


Figure 5-12. Rate of Lactonization for Six Syndiotactic Poly-(alkyl α-bromoacrylate) Esters in Solution at 80°C

Table 5-9. Effect of Tacticity on the Degree of Lactone Formation for Six Alkyl Esters After Lactonization for 4 Hours at 80°C.

Ester	Isotactic	Syndiotactic	Difference
Methyl	25	37	12
n-Pentyl	31	43	12
n-Butyl	32	45	13
Ethyl	33	47	14
n-Propyl	36	51	15
i-Propyl	39	55	16

alternately above and below the plane and positions the reacting groups in close proximity of each other.

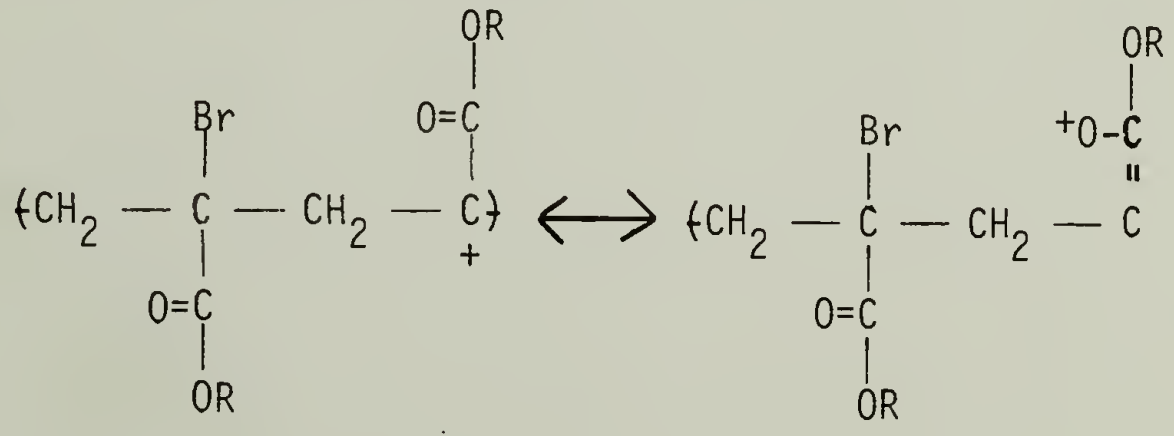
A maximum degree of lactone formation of 55% was exhibited by syndiotactic poly(i-propyl α-bromoacrylate). Conceivably, a higher conversion could be obtained at higher reaction temperatures if the competing side reactions could be kept to a minimum. One must also consider the influence of the rigid lactone rings which may well hinder lactonization at higher conversions. It is doubtful that lactone conversions above 50% could be achieved with the isotactic polymers due to the limitations imposed by the configuration.

An investigation on the solid state lactonization of stereoregular poly(α-chloroacrylic acid)[6] revealed the opposite effect of tacticity on lactone formation. They considered the polymer to exist in a 5_2 helical conformation. In this case, intramolecular lactone formation was facilitated by the isotactic configuration, although a difference of only a few percent was seen at 131°C. Unfortunately, the differences in the experimental conditions between their study and that here precluded the possibility for further comparison.

Several lactonization reactions were conducted with atactic poly-(t-butyl α-bromoacrylate), sample 53. In all cases the products became insoluble after approximately 15 minutes at 80°C in 1,1,2,2-tetrachloroethane. Insolubility occurred even sooner in the solid state reactions. The degree of lactonization was difficult to measure at reaction times in excess of a few minutes because of broadening in the infrared absorption bands. Presumably, this phenomenon resulted from crosslinking in the polymer (intermolecular lactonization) and the

insolubility of the polymers was excellent evidence for this. However, the degrees of lactonization measured were in the vicinity of 40% after 10 minutes at 80°C. This figure was significantly higher than any of the values determined for the other six esters. Syndiotactic poly-(i-propyl α-bromoacrylate), which displayed the largest degree of lactonization, produced only 20% lactone groups under identical conditions. Thus, it is reasonable to conclude that poly(t-butyl α-bromoacrylate) exhibited the highest tendency to lactonize of all the esters examined.

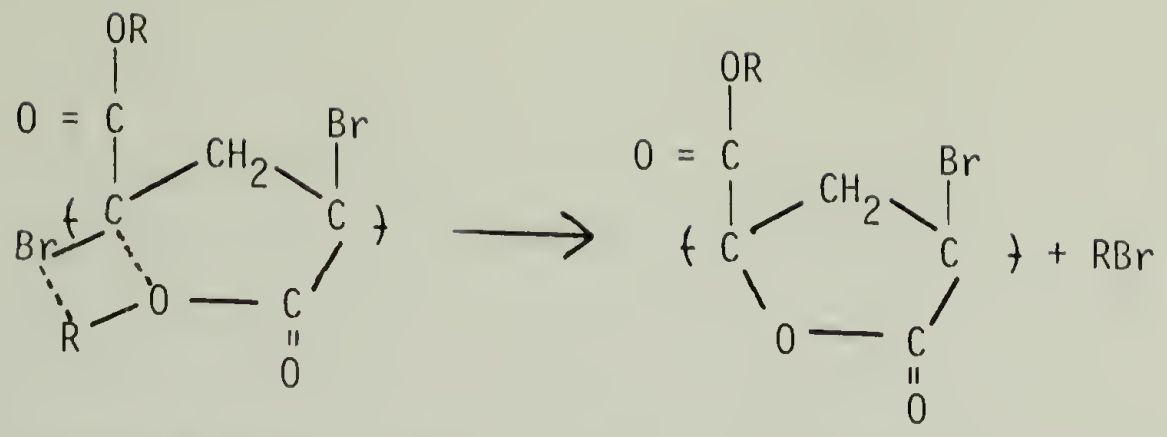
Possible mechanism. The lactonization reaction can be envisioned to occur by three different reaction pathways. These include an S_N1 type reaction, an S_N2 type reaction and concerted addition. It is unreasonable for the reaction to proceed through an S_N1 mechanism involving the formation of a carbonium ion at the quaternary carbon atom. The formation of such a tertiary carbonium ion is unfavorable because of the strong electron withdrawing effects of the carbonyl group. Once formed, the cation would be destabilized by the ester group, since delocalization of electrons would result in a resonance structure containing a positive, single bonded oxygen.



On the other hand, a carbon atom located adjacent to both a halogen and a carbonyl function display an enhanced reactivity towards nucleophilic attack (S_N^2). The electron attracting characteristics of the carbonyl group renders the α-carbon slightly positive and therefore it is more susceptible to nucleophilic attack. It is doubtful that the ester oxygen could function as a suitable nucleophile since it is not sufficiently basic (bascisity increases with the compounds ability to donate an electron pair). Moreover, this type of reaction is usually very dependent upon steric effects where lower reactivities are encountered with the bulkiest groups. The opposite effect was observed here since both the i-propyl and t-butyl esters displayed higher reactivities than all of the other esters.

Compared to the ester function, the carboxylic acid would be a much better nucleophile. The elimination of hydrogen bromide from the polymer could catalyze de-esterification and produce the carboxylic acid. Evidence for the formation of hydrogen bromide was substantiated by the appearance of an absorption band at 1600 cm^{-1} in the infrared spectrum of poly(ethyl α-bromoacrylate), Figure 5-5. This band was attributed to carbon-carbon double bonds. However, the formation of the acid was questionable since an absorption in the 3100 cm^{-1} region, indicative of the carboxylic acid hydroxyl group, was absent.

The third pathway involving concerted addition emerges as the most viable. In this type of mechanism, bond breakage and bond formation would occur at the same time. The following molecular representation depicts a possible model for the transition state which leads to the production



of a γ-lactone ring. The coordination suggested in this model may have some characteristics of a donor-acceptor complex. This complex would consist of an electron rich compound, the donor, and an electron poor compound, the acceptor. In this particular case the donor would be the O-R bond and the acceptor would be the C-Br bond. Although this process was probably not the driving force for the reaction, it may well have assisted in the coordination process.

The ability of the R group to function as a leaving group will dictate the extent of the reaction. In other words, the easier the O-R bond is to break, the more favorable will be the reaction. This statement is consistent with the fact that the i-propyl ester displayed the highest reactivity towards lactone formation as presented in Table 5-9. The breaking of the O-R bond would require the formation of the i-propyl cation and even though it would be exceedingly short lived, it would be partially stabilized by the electron donating effects of the two methyl groups. The linear esters cannot benefit from this stabilization. The high reactivity of the t-butyl cation toward the intermolecular reaction was also understandable since the t-butyl cation would be similarly stabilized.

It is important to point out that the lactonization reaction occurred primarily because of the relatively weak C-Br bond. The fact

that lactonization was not observed with the corresponding α-chloroacrylates is reflected by the higher strength of the C-Cl bond (81 versus 68 K/cal)[9].

The proposed mechanism is also consistent with previous lactonization studies on poly(α-bromoacrylic acid)[6]. Poly(α-bromoacrylic acid) exhibits an exceptionally high reactivity towards lactonization as compared to any of the α-bromoacrylate esters studied here. The coordination between the proton of the carboxylic acid function and the bromine should occur rather easily and therefore should lead to a high rate of lactone formation.

Kinetic measurements were obtained for the lactonization reactions of both the isotactic and syndiotactic polymers. The results of this analysis are exhibited in Figure 5-13 for the methyl and n-propyl esters. Both esters displayed first-order kinetics as evidenced by the linear plots for reaction times up to 120 minutes. The non-linearity observed after this time might have resulted from the increased backbone rigidity introduced by each successive lactone structure. At sufficiently high degrees of lactone formation, the added backbone stiffness could have hindered further lactonization.

From Figures 5-11 and 5-12 it is evident that reaction conversions of much greater than 50% were not possible at reasonable reaction times. The rate of the reaction should slacken off considerably as this point is approached. Furthermore, at longer reaction times, the intermolecular crosslinking reaction becomes increasingly important (see molecular weight section). The occurrence of this reaction would also

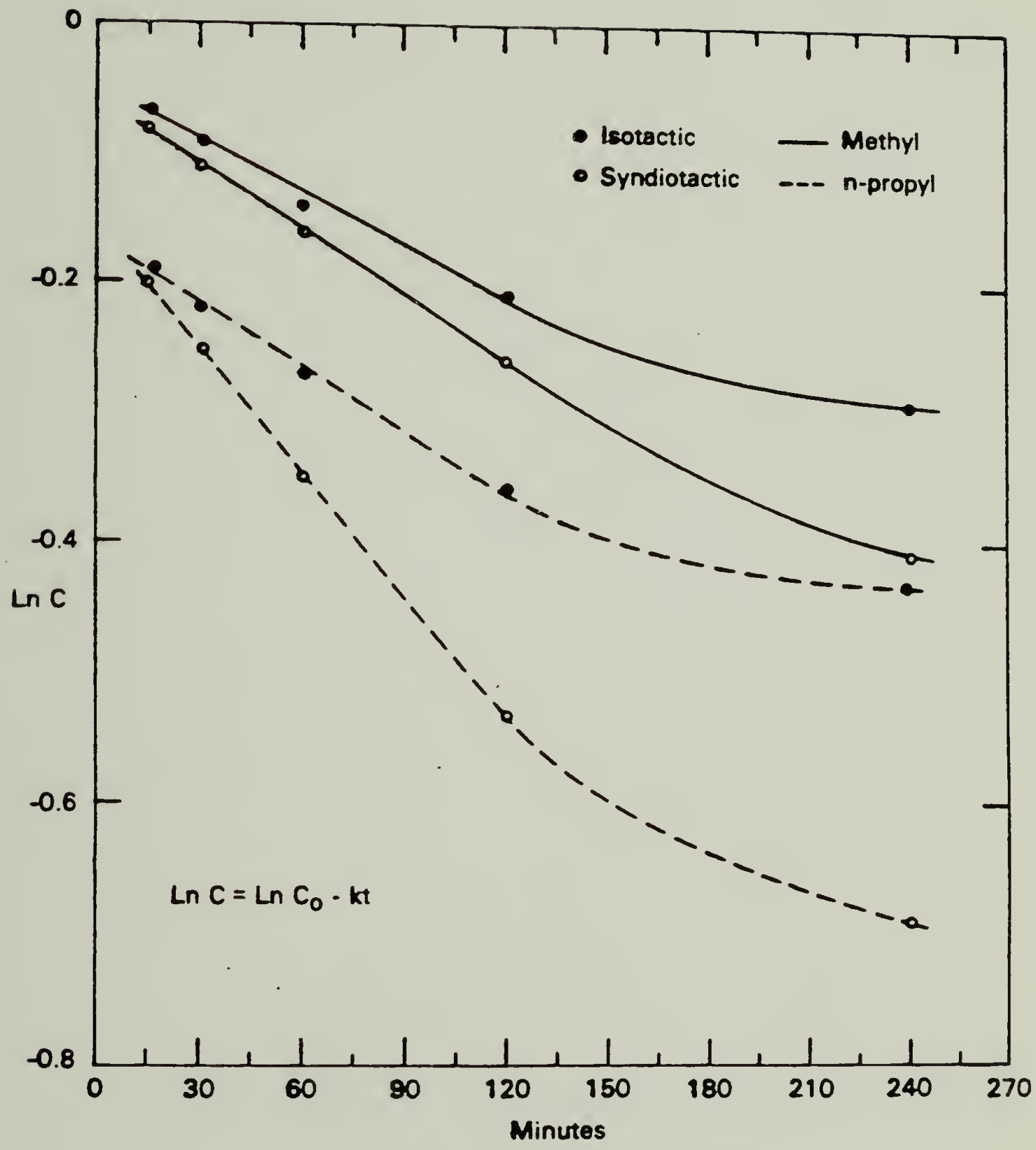


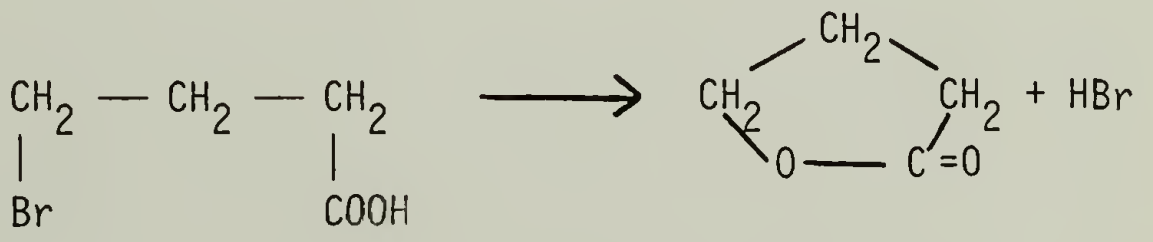
Figure 5-13. First-Order Kinetic Plots for Isotactic and Syndiotactic Poly(methyl α-bromoacrylate) and Poly-(n-propyl α-bromoacrylate)

function to restrict the motion of the chain and further retard lactonization.

Figure 5-14 displays the first-order plots for all of the syndiotactic esters. It is interesting that the non-linearity occurred at about 30 minutes for the i-propyl ester as compared to 120 minutes for the remaining esters. The degree of lactone formation was almost 50% (47%) for this ester after 30 minutes. The non-linearity observed after this point can be attributed to the inability of the polymer chain to form the dilactone repeat unit.

The measurement of first-order kinetics for ring closure reactions of this nature are not uncommon. Uncatalyzed cyclization reactions from haloamines of the following type, $X\text{-}(CH_2)_nNH_2$ were found to be strictly first-order[9-11]. The highest rate of cyclization was observed with the formation of five-membered rings. A study on the epoxidation of several ethylene halohydrins under both neutral and acid conditions also revealed first-order kinetics[12,13].

A first-order reaction rate was measured for the lactonization of γ-bromobutyric acid in neutral solution[14].



The authors spectulated that the rate of lactonization was determined by the uni-molecular ionization of the bromide ion. It seems unlikely

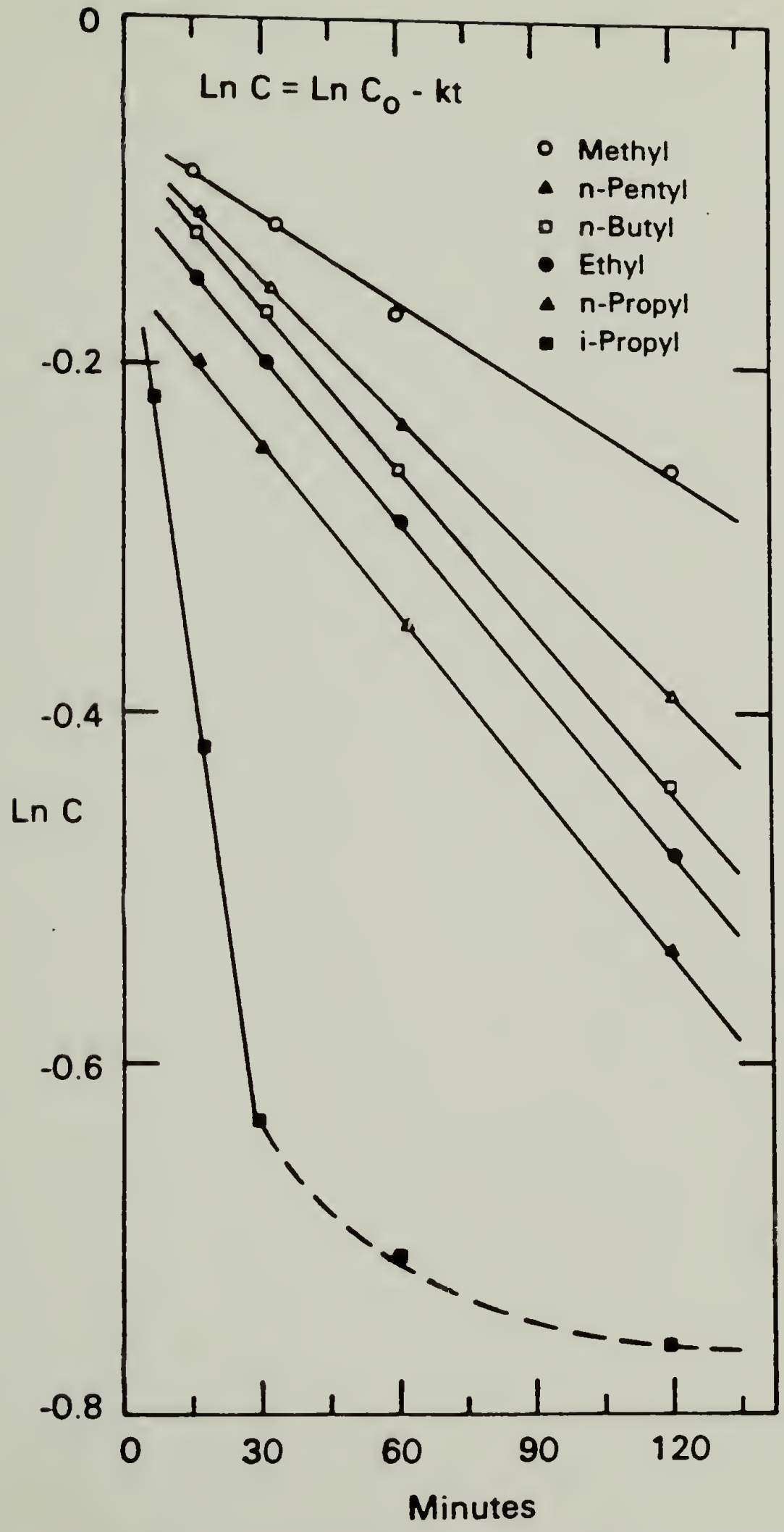


Figure 5-14. First-Order Kinetic Plots for All the Syndiotactic Esters

that this type of mechanism was operating in the lactonization of the poly(alkyl α-bromoacrylate)s in this investigation due to the reasons discussed in the early part of this section.

Summary and Conclusions

Lactonization studies were conducted with all of the poly(alkyl α-bromoacrylate) esters at temperatures from 70 to 150°C. The lactonization reactions were accompanied by the loss of the appropriate alkyl bromide, i.e., methyl bromide for poly(methyl α-bromoacrylate). The lactonization product was identified for the methyl, ethyl, n-propyl, and i-propyl esters by 90 mHz NMR spectroscopy and for the ethyl and n-propyl esters by pyrolysis gas chromatography. Evidence for lactone formation was also observed for all of the esters by IR spectroscopy. Upon heating, the polymers developed an absorption peak at 1798 cm^{-1} which was attributed to the lactone carbonyl group. This absorption band was used in conjunction with the ester carbonyl absorption band at 1730 cm^{-1} to quantitatively determine the degree of lactone formation.

The order of lactone formation increased in the following order: methyl, n-pentyl, n-butyl, ethyl, n-propyl and i-propyl. All of the syndiotactic polymers exhibited significantly higher lactonization rates under the same conditions. In general, the difference in lactone contents was between 12 and 16% for an isotactic-syndiotactic pair depending on the ester group. The difference in reactivity for the two different configurations was explained by the relative positions of the two reacting groups, the bromine atom and the ester group. The syndiotactic configuration allowed for a closer contact between these

two groups than the isotactic configuration. Analysis of the appropriate molecular models confirmed this rationale.

Slightly lower rates of lactone formation were observed when the identical lactonization reactions were conducted in the solid state. For instance, atactic poly(ethyl α-bromoacrylate) displayed a lactone content of 18% less in the solid state as compared to that in 1,1,2,2-tetrachloroethane after 4 hours at 80°C. The higher degree of lactone formation for the solution reactions was ascribed to the increased chain mobility in the solution state.

Determination of the molecular weights and molecular weight distributions before and after lactonization revealed that the intermolecular reaction was more prevalent in the isotactic samples than in the corresponding syndiotactic samples. The intermolecular crosslinking reaction was also found to be most important in the solid state reactions. When the intermolecular reaction occurred to any great extent, the polymers became insoluble. Poly(t-butyl α-bromoacrylate) exhibited the greatest tendency to undergo the intermolecular reaction since it became insoluble after only short reaction times. Infrared spectroscopy measurements indicated that the degree of lactone formation was close to 50% just prior to insolubility.

A mechanism involving a concerted, one-step reaction was proposed to explain the reactivities of the different ester groups. The lactonization reactions clearly followed first-order kinetics for reaction times of 120 minutes or less. This kinetic order was consistent with other similar ring closure reactions. The driving force

for the reaction was the attainment of a thermodynamically stable 5-membered lactone ring.

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CHAPTER VI

SUGGESTIONS FOR FUTURE WORK

The lactonization of the poly(alkyl α-bromoacrylate)s is one area which deserves further consideration. Additional investigations could be conducted along several directions. Of foremost importance would be the elucidation of the mechanism operating in the lactonization reaction. The effect of different solvents on the reaction could be studied, although they might be restricted to the atactic and syndiotactic samples due to the limited solubility of the isotactic polymers. The ability of different solvents to produce specific polar interactions may influence the rate of lactone formation. The effect of the solvent on the reaction kinetics might also lead to interesting results. The presence of acidic, basic or polar compounds during the lactonization reaction could produce effects to aid in the further understanding of the lactonization process. In addition, the effect of tacticity on lactone formation in the solid state as well as the kinetics of the process could yield substantially different results than were observed in solution.

It would be desirable to investigate the effect of different ester groups. For instance, the chloromethyl ester polymer, poly(chloromethyl α-bromoacrylate) might behave differently than the methyl ester, poly-(methyl α-bromoacrylate). The study of inductive or polar effects of various ester groups may also contribute to the further understanding of the reaction mechanism.

It would be very desirable to study the lactonization process by ^{13}C nuclear magnetic resonance spectroscopy. The chemical shifts will be different for both the carbonyl and quaternary carbon resonances of the unreacted and reacted (lactonized) polymers. If a sufficient chemical shift change occurs, one may be able to differentiate between the regular lactone unit, the dilactone unit (if it exists) and the intermolecular crosslinking unit. The extent of the intermolecular crosslinking reaction could be determined and compared for the reactions conducted in both solid state and solution. Possibly, the intermolecular reaction could be significantly decreased if the reactions were conducted in very dilute solution. Although a 19 mHz ^{13}C NMR spectrometer was sufficient for this investigation, a higher field instrument could be required for experiments of this nature.

The effect of lactonization on the crystallinity and crystalline morphology of the stereoregular alkyl α-bromoacrylate polymers could be investigated. Studies of this nature have not been conducted for any poly(alkyl α-bromoacrylate)s of this or any other investigation. It may be possible to orient the polymers and then study this effect on the rate of lactone formation. Unfortunately it would not be feasible to employ any type of thermal annealing to increase the degree of crystallinity.

Additional ^{13}C NMR studies of the poly(alkyl α-bromoacrylate)s could be advantageous if the lactonization reaction could be inhibited. The experiments could then be carried out at elevated temperatures. At a temperature such as 120°C, the resolution of the resonance peaks

should increase and much better solubility would result for the isotactic polymers. As a result, less error would be involved in measuring the tacticity.

The initial objective of the present investigation was to synthesize a series of high molecular weight, highly stereoregular poly(alkyl α-bromoacrylate)s where the influence of the steric structure on the glass transition temperature could be evaluated. Because of the low thermal stability of the polymers, all attempts to measure the glass transition temperatures failed. In an effort to continue with the original objective, several other disubstituted acrylates could be chosen.

The poly(alkyl α-bromomethylacrylate) series would be a logical choice for several reasons. First of all, the polymerization techniques employed for the preparation of the isotactic poly(alkyl α-bromoacrylate)s could be utilized successfully in the polymerization of the alkyl α-bromomethylacrylates. Once polymerized, the polymers should remain thermally stable to well above their glass transition temperatures since they would not be expected to undergo lactonization. The thermal stability of the polymers would allow for the determination of polymer tacticity by ^{13}C NMR spectroscopy at elevated temperatures. The evaluation of tacticity would be analogous to that of the poly(alkyl α-bromoacrylate)s. The thermal relaxation behavior of the polymers could be studied by dynamic mechanical and dielectric relaxation methods. Also, the glass transition temperature can be obtained by these techniques.

The poly(alkyl ethacrylate) series could be studied with the same purpose in mind. As a matter of fact, any of the poly(alkyl α-alkacrylate)s could be chosen. All of these series would be similar to the poly(alkyl methacrylate) series and therefore the stereoregular polymers could be synthesized with little difficulty. The determination of polymer tacticity should be possible with ^{13}C NMR spectroscopy. Furthermore, the polar factors which were present in the poly(alkyl α-chloroacrylate)s will be completely absent in these polymers.

A P P E N D I X

THE SYNTHESIS AND POLYMERIZATION OF ALKYL(α-PHENOXYMETHYL) ACRYLATES

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Introduction

As part of a continuing program in this laboratory on the study of structure-property relationships in polymers from α,α-distributed ethylene monomers (principally acrylates)[1], we have initiated an investigation on the synthesis and controlled polymerization of methacrylate-type monomers containing substituents on the α-methyl position. The first such monomer investigated is that containing the phenoxy group, and the present report concerns the synthesis, preparation, structure and properties of the methyl and ethyl ester derivatives of these (α-phenoxymethyl) acrylates:

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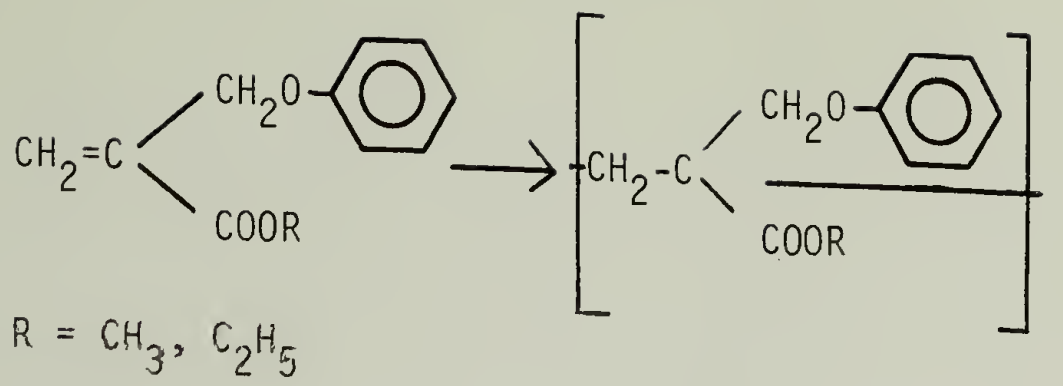
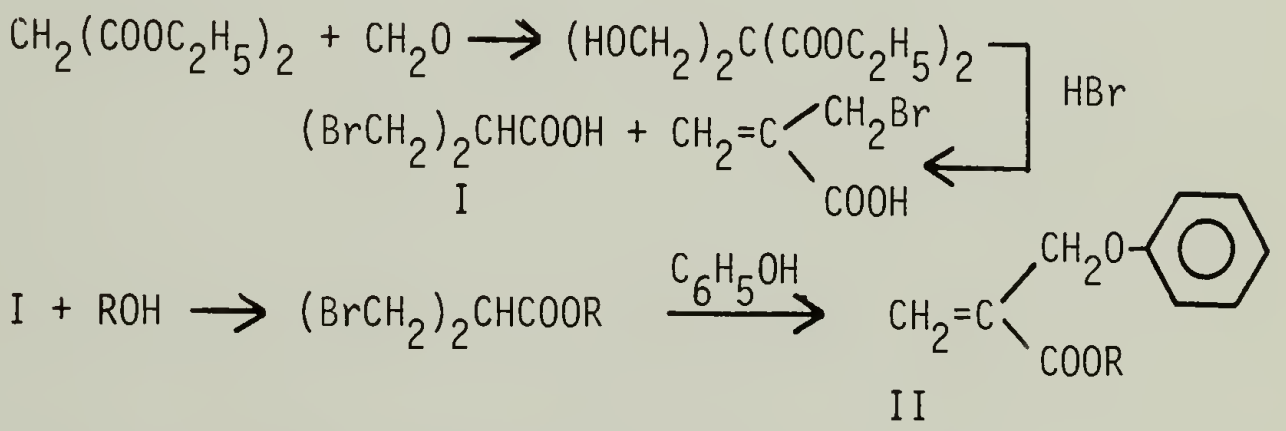


Reports of other monomers in this series will be made in the future.

Monomer Preparation

The monomers were prepared in good overall yield starting from the condensation of ethyl malonate with formaldehyde and reacting the bis(hydroxymethyl) derivative so formed with hydrogen bromide to generate a mixture containing approximately 75 mole % of the desired bis(bromomethyl) compound, I, and 25% of the interesting reactive monomer (α-bromomethyl)acrylic acid, as follows:



Intermediate I could be readily esterified in alcoholic sulfuric acid solution, and the ester was converted directly to the desired monomer, II, by reaction with phenol in a solution of sodium hydroxide in methanol. Monomer structures were verified by NMR analysis.

Polymer Preparation and Properties

In an attempt to prepare polymers of different tacticities, the methyl and ethyl ester derivatives of II were polymerized at two different temperatures, 60° and -50°C, by free radical initiators. For the former, azobisisobutyronitrile was used in toluene solution, while for the latter, irradiation of the monomer in tetrahydrofuran with ultraviolet light in the presence of benzoin was used. Polymer yields were approximately 10% in the former and 25% in the latter for both monomers. Results from the characterization of the methyl and ethyl ester polymers obtained from the high and low temperature polymerization reactions are collected in Table 1, including both molecular weight measurements by gel permeation chromatography and tacticity determination by NMR.

The relatively low yields and molecular weights obtained are most likely a reflection of the low ceiling temperatures of polymerization to be expected for these sterically-hindered monomers, although the molecular weights were not significantly affected by changes in polymerization reaction temperature. That is, a decrease in reaction temperature of 110°C (from 60° to -50°C) did not result in an increase in molecular weight for either ester monomer, although some increase in yield was obtained.

Polymer tacticity. Quite remarkably, as shown by the data in Table 1, no change in tacticity was observed either between the polymers prepared at 60° and -50°C. At both temperatures, almost perfectly atactic polymers were obtained.

Table 1. Characterization of Methyl and Ethyl (α-Phenoxymethyl)acrylate Polymers

Monomer	Temp., °C	Molecular Weight[a] Mn	Mw	Mw/Mn	Tacticity, triad%[b] I	H	S	T_g, °C
methyl	60	4600	9,400	2.04	23	49	28	114
	-50	4400	9,200	2.08	--	--	--	112
ethyl	60	5900	10,400	1.75	--	--	--	86
	-50	6200	10,300	1.68	25	47	28	90

[a]As determined by GPC relative to polystyrene standards.

[b]I-isotactic, H-heterotactic, S-syndiotactic triads.

The undecoupled ^{1}H NMR spectrum of poly(ethyl α-phenoxymethyl) acrylate was not sensitive to the stereoregularity of the polymer and gave no information on the tacticity. The resonances of the carbonyl carbon in this polymer split into three peaks (Fig. 1) and the ^{13}C-spin-lattice relaxation time, ^{13}C-T_1, for these three peaks increased in the order of increasing magnetic field as shown in Table 2. Previous investigations have revealed that the carbons in isotactic poly(α-substituted acrylate)s always show longer T_1's than those in the corresponding syndiotactic ones; that is the T_1 value should be in the order of isotactic > heterotactic > syndiotactic triads[2]. Hence, on this basis, it is possible to assign the carbonyl carbon peaks to syndiotactic, heterotactic and isotactic triads with increasing magnetic field. The intensity measurement of the peaks indicated that the tacticity of the polymer is I 25%, H 47% and S 28% (Table 1). Because the polymers were almost perfectly atactic, with syndiotactic and isotactic triad contents being essentially identical; however, the assignment order made little difference as long as the heterotactic peak was selected as the central one.

The tacticity sequence of the chemical shifts of the carbonyl carbon atoms was the same as that observed in poly(methyl methacrylate)[13] but opposite to that in the poly(α-chloroacrylate)s[31]; that is, the sequence in the present case was syndiotactic < heterotactic < isotactic triads with increasing field strength.

The resonance of the C-1 carbon in phenyl ring also split into three peaks which were assigned to syndiotactic, heterotactic and

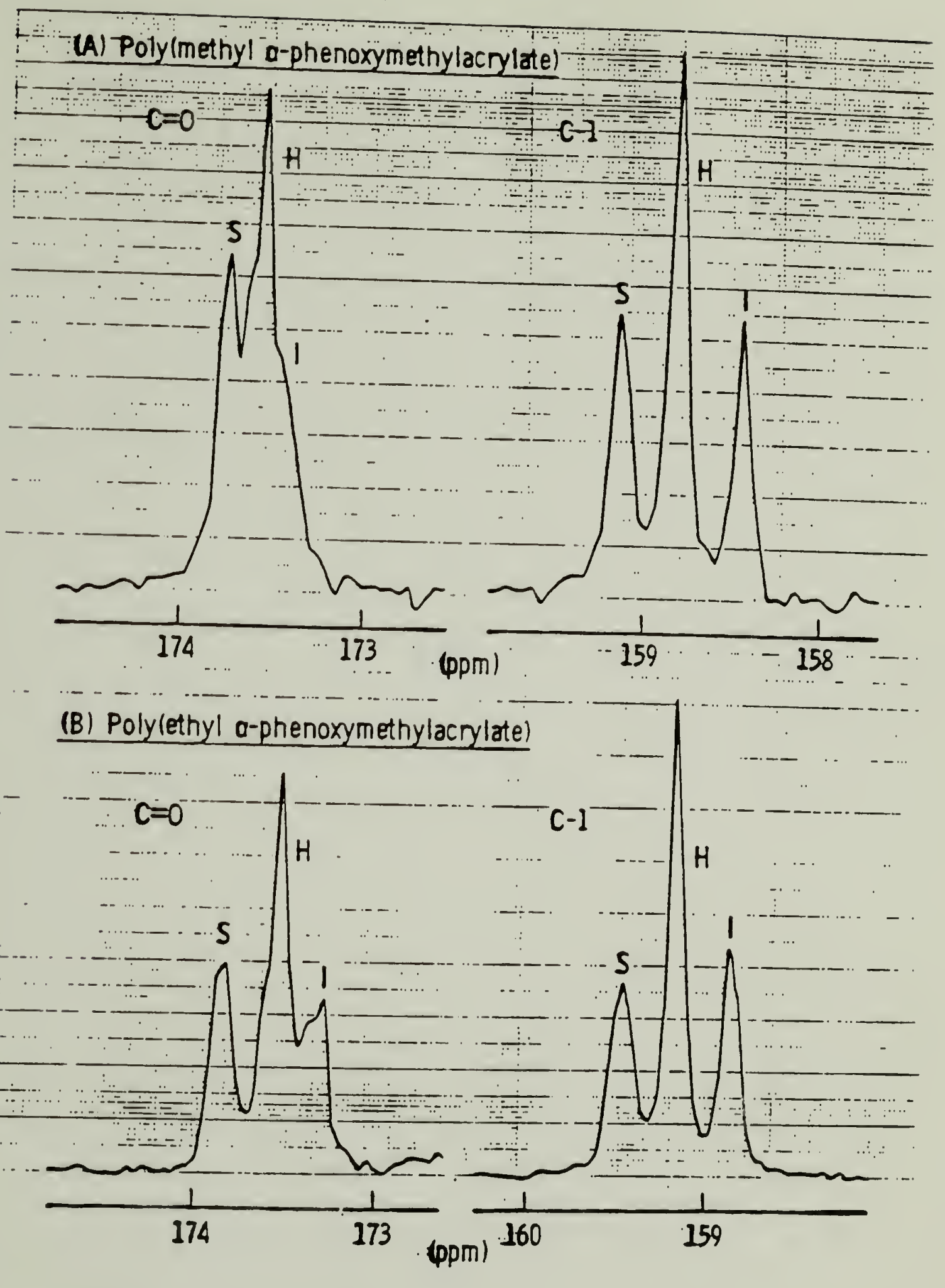


Fig. 1. ^{13}C NMR spectra of carbonyl and C-1 (phenyl) carbons in (A) poly(methyl α-phenoxymethylacrylate) and (B) poly-(ethyl α-phenoxymethylacrylate) measured in toluene-d_8 (1.0 mole/l) at 25 MHz and 110°C. (A) 2000 scans, (B) 1700 scans.

isotactic triads with increasing magnetic field by the comparison of the relative intensities of the peaks with those of the carbonyl peaks. The tacticities determined from the carbonyl and the C-1 resonances are in good agreement.

In the ^{13}C NMR spectrum of poly(methyl α-phenoxymethylacrylate) the resonances of the carbonyl carbon and the C-1 carbon in the phenyl ring also split into three peaks, respectively. The peaks in the carbonyl resonance were not well separated and the highest field peak appeared as a shoulder. The T_1 for the lowest field peak was shorter than that for the central one (Table 2). So the peaks should be assigned in the same order as the peaks of the carbonyl carbon in the poly(ethyl α-phenoxymethylacrylate). The three peaks in the C-1 carbon resonance were well resolved and could be assigned to syndiotactic, heterotactic and isotactic triads in the order of increasing magnetic field similar to those in the poly(ethyl α-phenoxymethylacrylate). The tacticity of the polymer was also completely atactic.

The ^{1}H NMR spectrum of poly(methyl α-phenoxymethylacrylate) is shown in Figure 2. The methoxyl methyl protons show three peaks at 3.24, 3.12 and 2.98 ppm, which could be assigned to syndiotactic, heterotactic and isotactic triads with increasing magnetic field by the comparison of the spectrum with the ^{13}C NMR spectrum. The small splitting in the heterotactic peak should be due to the tactic pentad structures. The agreement of triad amount between the ^{13}C and ^{1}H measurements was within 3 to 4% of each other.

Table 2. NMR Analysis of Methyl and Ethyl (α-Phenoxymethyl)acrylate Polymers

Ester Monomer	Assignment	Chemical Shift, ppm			T_1, m sec		
		I	H	S	I	H	S
methyl	^1H, OCH_3	2.98	3.12	3.24	--	--	--
	^{13}C, C=O	--	173.75	173.94	--	1906	1701
	^{13}C, C-1	158.64	158.98	159.32	--	--	--
ethyl	^{13}C, C=O	173.31	173.55	173.85	1801	1735	1534
	^{13}C, C-1	158.89	159.18	159.47	--	--	--

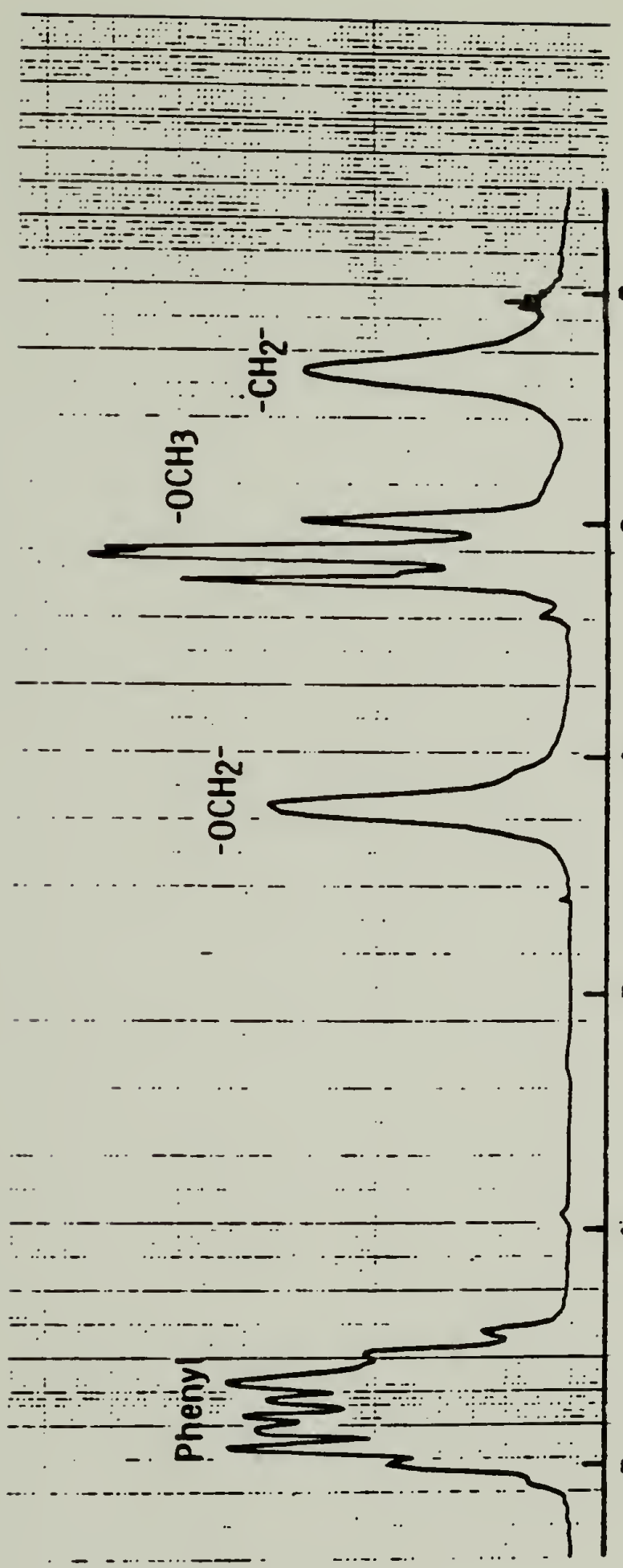


Fig. 2. ^{1}H NMR spectrum of poly(methyl α-phenoxymethylacrylate) measured in toluene-d_8 (0.5 mole/l) at 100 MHz and 110°C.

Glass transition temperature. Glass transition temperatures, T_g, as determined by differential scanning calorimetry, DSC, for the two different ester polymers are collected in Table 1. The T_g values were essentially identical within each ester polymer for the polymers prepared either at high or low temperatures because the polymers did not vary in molecular weight or tacticity as a function of polymerization temperature[1]. As expected, T_g values of the methyl ester polymer were considerably higher (even at lower molecular weights) than those of the related ethyl ester polymers because of the generally observed increasing internal plasticization by the ester group with increasing size of the alkyl group[4].

Conclusions

Polymers with almost perfectly atactic structures are uncommon, but such structures have been reported for the free radical polymerizations of methyl acrylate[5], ethyl acrylate[6], vinyl chloride[7], acrylonitrile[8], and vinyl acetate[9]. Trimethylsilyl acrylate also gave atactic polymers at higher polymerization temperatures[6]. In the free radical polymerization of α,α-disubstituted olefin monomers, such as methyl methacrylate[10] and α-methylstyrene[11], syndiotactic polymers are usually obtained, although the fractions of heterotactic triads in these products generally increase with increasing polymerization temperatures.

Large substituents at the α-position of acrylate monomers have been shown to favor the formation of atactic polymers and, as shown

by one of us, methyl α-phenylacrylate gave an almost perfectly atactic polymer by free radical as well as by anionic polymerization[12]. As discussed previously, the formation of an atactic polymer indicates that the steric and polar interactions of the two α-substituents are nearly equal in the stereoregulating step; that is, in the formation of the new tetrahedral center in addition to the next monomer unit[12]. In the present case, the insensitivity of tacticity to polymerization temperature specifically indicates that the activation energies for syndiotactic and isotactic addition were the same and were independent of ester type.

As expected for the presence of the large α-phenyl substituent, the glass temperatures of these polymers were quite high and were higher than those of either methacrylate or chloroacrylate polymers. For example, at comparable molecular weights, the glass temperature of poly(ethyl α-chloroacrylate) having a triad tacticity distribution of 31% I, 44% H and 25% S was 70°C[1] compared to 90°C for poly(ethyl α-phenoxymethylacrylate) of 25% I, 47% H and 28% S.

Atactic poly(methyl α-phenoxymethylacrylate) and poly(methyl α-phenylacrylate) had glass temperature of 117 and 118°C, respectively, but the latter polymer may have been of higher molecular weight[12]. In contrast, poly(methyl α-benzylacrylate) was observed to have essentially the same glass temperature, of approximately 45°C, as poly(methyl methacrylate) at a similar tacticity and molecular weight. Unfortunately, both tacticity and molecular weight have a very strong effect on this property, and more careful comparisons of samples of different polymers with identical structural characteristics must be made.

Experimental

Dimethyl bis(hydroxymethyl)malonate. In a 1-liter beaker, 90 g (3 m) of formaldehyde was combined with 8 g of K_2CO_3, followed by the addition of 160 g (1 m) of diethyl malonate while maintaining the temperature below 20°C to prevent polymerization of formaldehyde. After one hour of stirring, the reaction contents were transferred to a separatory funnel containing 320 ml of a saturated ammonium sulfate solution and shaken well. To this mixture was added 320 ml of diethyl ether, the ether layer was separated and dried over 20 g of anhydrous Na_2SO_4, ether and excess formaldehyde were distilled off, and the residual liquid was placed in an ice-bath until the product crystallized (2-3 hours). Isopropyl ether (500 ml) was added and the mixture was warmed to 50°C until the product dissolved. The solution was transferred to a flask, stirred in an ice-bath until a thick suspension of crystals formed and left there for an additional two hours. After the white product was filtered and dried in a vacuum for 24 hours, a melting point of 40-50°C was observed. The yield was 165 g or 75%. Recrystallization from isopropyl ether gave a product melting at 50-51°C.

β,β'-Dibromoisobutyric acid. One mole (220 g) of the product from above and 800 ml (7 m) of a 48% hydrobromic acid solution were combined in a 2 liter, one neck boiling flask and heated until ethyl bromide began to distill from the reaction mixture. After this liquid ceased to distill, the reaction mixture was refluxed for six hours. Subsequently, the product was crystallized from solution in an ice-bath for three hours. The solid was filtered, washed with ice water and dried as

before. A second fraction of crystals was obtained by removing approximately 400 ml of liquid from the filtrate and repeating the crystallization. Crops of 120 and 50 g resulted in a combined yield of 70%, with a melting point of 101-103°C.

Methyl β,β'-dibromoisobutyrate. This esterfication reaction was carried out by combining 246 g (1 m) of the acid from above, 250 ml of methanol and 2 ml of concentrated sulfuric acid, in a round-bottom flask. After 12 hours of reflux, the reaction mixture was extracted with 100 ml of water. The non-aqueous layer was dried over anhydrous sodium sulfate, filtered and subjected to distillation to remove the alcohol. The remaining liquid was distilled under a reduced pressure of 5 mm Hg, giving a colorless liquid boiling at 70-72°C in a 70% yield.

Methyl (α-phenoxymethyl)acrylate. The previous product (0.5 m) was added slowly to a solution of sodium hydroxide (1 m) and of phenol (1 m) in 200 ml of methanol. After six hours of stirring at room temperature, methanol was removed by normal distillation. The residual liquid was extracted with 200 ml of diethyl ether, washed with 50 ml of a 10% sodium hydroxide solution, 50 ml of water and dried over anhydrous magnesium sulfate. Removal of the ether after filtration left a colorless liquid in 85% yield; boiling point 85°C/2 mm. The boiling point of the ethyl ester was 94°C/2 mm. Elemental analysis of the two esters were as follows: methyl ester, Calcd. 68.73%, 6.30%; Obsvd. 67.69% C, 6.54 H; ethyl ester, Calcd. 69.88% C, 6.84% H; Obsvd. 67.88% C, 7.18 H.

Acknowledgement

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